The transformation of the magnetostructural phase transition with Ti addition in Gd$_5$Si$_2$Ge$_2$

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Abstract. The magnetic, thermal expansion and magnetostriction measurements of Gd$_{5-x}$Ti$_x$Si$_2$Ge$_2$ (x=0, 0.05, 0.1) compounds have been carried out in wide range of fields and temperatures. It is found that Ti addition leads to the disappearance of the structural transformation, the change of the order of the phase transition and the decrease of the hysteresis. The large positive magnetostriction associated with the structural phase transition in Gd$_5$Si$_2$Ge$_2$ changes to the small negative one associated with the magnetic phase transition in Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$. The linear dependence of volume magnetostriction on the square of magnetization obtained for all investigated compounds is explained using the thermodynamic theory.

1 Introduction

The Gd$_5$Si$_2$Ge$_2$ compound has attracted the considerable attention since it exhibits the giant magnetocaloric effect (MCE) [1,2]. The structural and magnetic transformations occurring simultaneously at Curie temperature lead to the first order phase transition from paramagnetic monoclinic state to ferromagnetic orthorhombic state. At the same time, the large magnetic and thermal hysteresis typical to the first order phase transitions leads to the difficulties in possible practical application of this compound. Therefore the great interest presents the search of optimal substitution in p- or 4f-sublattice for reduction of hysteresis. The influence of small Sn and In substitutions on the magnetostructural phase transitions have been studied in detail [3-5]. These studies have shown that the Curie temperature slightly shifts by not more than 10 K, the first order phase transition is preserved and MCE slightly increases with small p-element addition. However, the hysteresis losses also increase. In this work the magnetic, thermal expansion and magnetostriction measurements of Gd$_{5-x}$Ti$_x$Si$_2$Ge$_2$ (x=0, 0.05, 0.1) compounds have been carried out in order to determine the influence of the temperature and magnetic field on the magnetoelastic properties of these alloys.

2 Experimental details

The Gd$_{5-x}$Ti$_x$Si$_2$Ge$_2$ (x=0, 0.05, 0.1) samples were prepared by arc-melting in an electric arc furnace under an argon atmosphere using a non-consumable tungsten electrode and a water-cooled copper tray. The ingots were remelted three times to insure homogeneity. The arc-melted samples were annealed at 970 K for 300 h in an argon atmosphere and quenched in ice-cold water. The quality of the samples was evaluated using X-ray diffraction and electron microprobe analysis.

The field and temperature dependencies of magnetization M were measured in applied magnetic fields up to 12 kOe in the temperature range 80–340 K both upon heating and upon cooling. The thermal expansion and magnetostriction measurements were carried out using the strain gauge method in static magnetic fields up to 12 kOe in the temperature range 80–330 K. The magnetostriction measurements were carried out under isothermal conditions.

3 Results

X-ray diffraction at room temperature and electron microprobe analysis reveal that all compounds contain a small amount of impurity GdGe-type phase. The main phase in Gd$_5$Si$_2$Ge$_2$ is monoclinic Gd$_5$Si$_2$Ge$_2$-type phase (space group P112$_1$/a) whereas in Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$ it is orthorhombic Gd$_5$Si$_4$-type phase (space group Pnma). Gd$_{4.95}$Ti$_{0.05}$Si$_2$Ge$_2$ contains both Gd$_5$Si$_2$Ge$_2$-type and Gd$_5$Si$_4$-type phases. The lattice parameters and unit cell volume are listed in Table 1.

According to the temperature dependences of magnetization, all investigated compounds demonstrate ferromagnetic behavior below Curie temperature T_C. The Curie temperatures determined from the maxima on $|dM/dT|$ curves are given in Table 2. For Gd$_5$Si$_2$Ge$_2$ the obtained Curie temperature is in a good agreement with

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the literature data [2]. The Ti addition shifts T_C to higher temperatures.

Table 1. The lattice parameters of monoclinic and orthorhombic unit cells for $Gd_{5-x}Ti_xSi_2Ge_2$ compounds.

x	a (Å)	b (Å)	c (Å)	γ (°)	V (Å³)
Monoclinic structure					
0	7.571 (1)	14.773 (3)	7.765 (1)	93.15 (1)	867.18
0.05	7.546 (6)	14.73 (1)	7.759 (5)	93.05 (7)	861.21
Orhtorhombic structure					
0.05	7.490 (4)	14.735 (6)	7.782 (3)	90	858.86
0.1	7.4965 (8)	14.758 (2)	7.7930 (9)	90	862.14

The Belov-Arrott plots (H/M vs. M^2) obtained from the magnetization curves are linear near T_C for compounds with x=0.05 and 0.1 which indicates that the phase transition is second order for substituted compounds. Whereas the H/M vs. M^2 curves are nonlinear for $Gd_5Si_2Ge_2$ since the first order phase transition occurs for this compound. With changing of the order of phase transition the value of the thermal hysteresis also decreases from 17 K for $Gd_5Si_2Ge_2$ to 5-7 K for substituted compounds.

Table 2. The magnetic and magnetoelastic properties of $Gd_{5-x}Ti_xSi_2Ge_2$ compounds. T_C is Curie temperature, ω_{max} and ω_{min} are the magnitudes of the positive and negative peaks on the temperature dependence of volume magnetostriction

x	cooling			heating		
	T_C (K)	ω_{max} (10^{-4})	ω_{min} (10^{-4})	T_C (K)	ω_{max} (10^{-4})	ω_{min} (10^{-4})
0	271	9.4		288	2.5	
0.05	296	2.0	-0.8	301	0.1	-1.2
0.1	292		-0.5	299		-0.4

Fig. 1 shows the results of thermal expansion measurements. Above T_C the thermal expansion is observed to increase almost linearly. $Gd_5Si_2Ge_2$ demonstrates the change in the thermal expansion of about 10^{-3} near T_C. It also exhibits the large thermal hysteresis of about 10 K. For $Gd_{4.95}Ti_{0.05}Si_2Ge_2$, the change in the thermal expansion is observed near 270 K upon cooling and near 285 K upon heating, which is considerably lower than T_C values obtained from magnetization data. The observed change is significantly lower in magnitude than that for $Gd_5Si_2Ge_2$. For $Gd_{4.9}Ti_{0.1}Si_2Ge_2$, the thermal expansion increases almost linearly with temperature in the entire measured temperature range, which indicates an insignificant contribution from the magnetic subsystem compared with the phonon contribution. The hysteresis is almost absent for this compound.
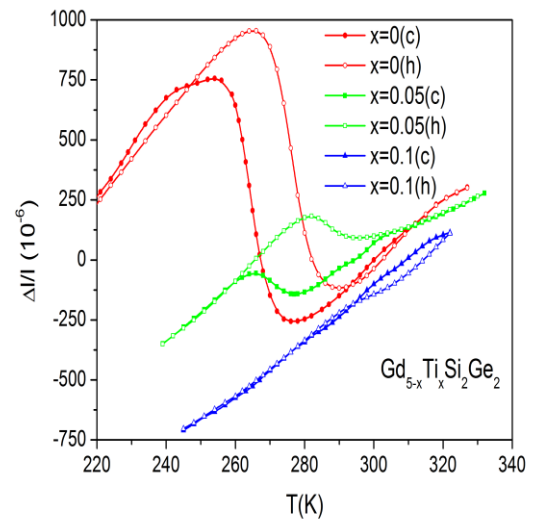

Fig. 1. The linear thermal expansion of $Gd_{5-x}Ti_xSi_2Ge_2$ compounds. Data obtained on continuous cooling (full symbols) and heating (open symbols).

Magnetostriction measurements revealed that the values of longitudinal $\lambda_\parallel$ and transverse magnetostriction $\lambda_\perp$ are almost the same. The volume magnetostriction was obtained as $\omega = \lambda_\parallel + 2\lambda_\perp$. The temperature dependences of volume magnetostriction in the applied field of 11.8 kOe are presented in fig. 2. The $Gd_5Si_2Ge_2$ compound possesses the large positive magnetostriction with the maximum near the Curie temperature. The ω values obtained upon cooling and upon heating are very different for this compound. The volume magnetostriction reaches 9.4×10^{-4} upon cooling and does not exceed 2.5×10^{-4} upon heating. For $Gd_{4.95}Ti_{0.05}Si_2Ge_2$, $\omega(T)$ has the positive peak near 280 K and the negative peak near 295 K. Below 290 K the hysteresis is very large while above 290 K the ω values obtained upon cooling and upon heating are rather close. The magnitude of positive peak is larger than that of negative peak but significantly lower than the maximal value for $Gd_5Si_2Ge_2$.
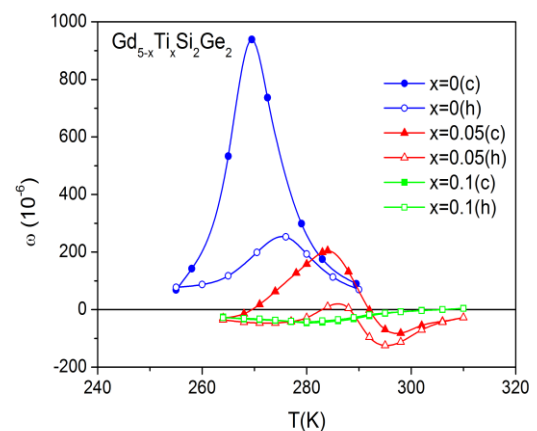

Fig. 2. The temperature dependences of volume magnetostriction for $Gd_{5-x}Ti_xSi_2Ge_2$ compounds in the applied field of 11.8 kOe. Data obtained on continuous cooling (full symbols) and heating (open symbols).

For Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$ the maghetostriction becomes negative. The small negative peak is observed near 280 K on $\omega(T)$ for this compound. The hysteresis is almost absent for Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$. The magnitude of the peak is much lower than that of negative peak for Gd$_{4.95}$Ti$_{0.05}$Si$_2$Ge$_2$.

4 Discussion

The obtained volume magnetostriction data points out that the maximal value of ω is observed in the vicinity of the magnetostructural phase transition in Gd$_5$Si$_2$Ge$_2$. This large positive magnetostriction is due to magnetostructural phase transition from paramagnetic monoclinic state to ferromagnetic orthorhombic state under the action of magnetic field. According to the thermodynamic relation [6,7]

$$\left(\frac{\partial \omega}{\partial H}\right)_P = -\left(\frac{\partial M}{\partial P}\right)_H, \quad (1)$$

where P is the applied pressure. The thermal expansion measurements revealed that the transition from paramagnetic monoclinic state to ferromagnetic orthorhombic state is accompanied by the abrupt increase in the sample size (see fig. 1). This effect can be considered as the negative pressure acting on the sample. So, the negative dP leads to the positive dM on cooling and conversely the positive dP leads to the negative dM on heating. Anyway, $(\partial M/\partial P)_H < 0$, thus $(\partial \omega/\partial H)_P > 0$. So, at the region of the structural phase transition the value of volume magnetostriction ω should increase with the applied magnetic field, which is observed in fig. 2.

For the ferromagnet in the magnetic field H and under the applied pressure P the thermodynamic potential G can be written as [6,7]

$$G = aM^2 + bM^4 + cP^2 - MH, \quad (2)$$

where a, b and c are the thermodynamic coefficients. According to Nikitin et al. [7]

$$a = a'(T - T_C) + \gamma P, \quad (3)$$

where γ is the magnetoelastic coefficient and a' is the thermodynamic coefficient at $P = 0$. The volume change ω can be found directly from the thermodynamic potential

$$\omega = \frac{\partial G}{\partial P} = \gamma M^2 + 2cP. \quad (4)$$

The equation (4) is valid for the second order phase transitions. The linear ω vs. M^2 plots obtained for Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$ (fig. 3b) confirm that the phase transition is second order for this compound. The volume magnetostriction also depends linearly on the square of magnetization for two other investigated compounds (fig. 3a). However, unlike Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$, for which ω vs. M^2 curves are almost parallel, in Gd$_5$Si$_2$Ge$_2$ and Gd$_{4.95}$Ti$_{0.05}$Si$_2$Ge$_2$ compounds the slope of the lines changes with temperature. It points to the change of the magnetoelastic coefficient γ, which is associated with the change of the compressibility of the sample due to the magnetostructural transition. Some deviation of ω vs. M^2 curves from the linear behavior is due to the contributions to the volume magnetostriction from terms with fourth and higher powers of M in the expansion of G into a power series of M.
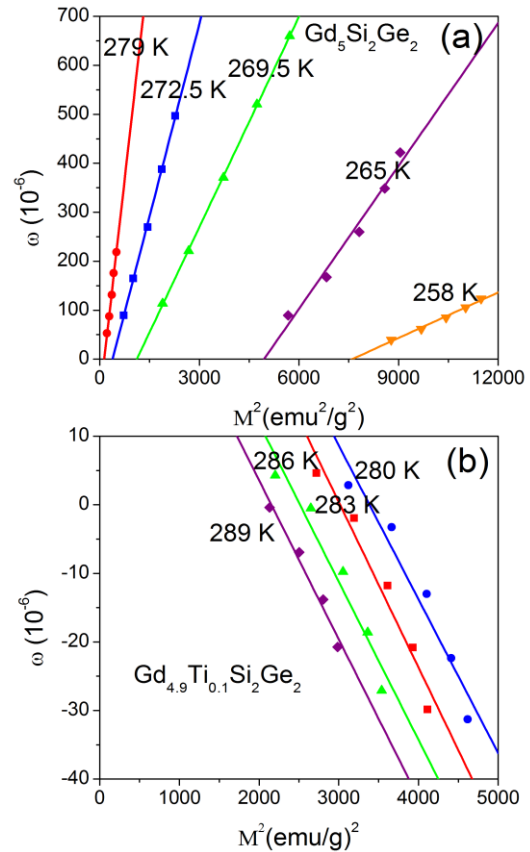

Fig. 3. The dependence of the volume magnetostriction on the square of magnetization for Gd$_5$Si$_2$Ge$_2$ (a) and Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$ (b)

The magnetostriction observed for the investigated compounds can be considered as the kind of the forced magnetostriction, which has the contributions from magnetostuctural phase transition and from the change of magnetization inside the magnetic domains under the action of field. As has been shown by Belov [6], the forced magnetostriction is connected to the exchange integral by relation

$$\frac{\partial \omega}{\partial H} = -\frac{T}{\kappa}\frac{1}{A}\frac{\partial A}{\partial \omega}\frac{\partial M_S}{\partial T}, \quad (5)$$

where κ is bulk modulus, A is the exchange integral, M_S is the spontaneous magnetization. The change of the sign of the volume magnetostriction of Gd$_{5-x}$Ti$_x$Si$_2$Ge$_2$ when x changes from 0 to 0.1 indicates the radical transformation of the magnetostructural state with Ti addition which is related with change of crystal structure from monoclinic to orthorhombic.

In Gd$_5$Si$_2$Ge$_2$ the temperature induced magnetostriction deformation due to the magnetostructural phase transition is added to the phonon part of the thermal expansion. For Gd$_{4.9}$Ti$_{0.1}$Si$_2$Ge$_2$, the structural phase transition is absent, therefore no noticeable anomalies are observed near the Curie temperature on the thermal expansion curve. In Gd$_{4.95}$Ti$_{0.05}$Si$_2$Ge$_2$ the orthorhombic and monoclinic phases are likely to coexist in the vicinity of the phase transition, which is also observed on the X-ray diffraction pattern for this compound. The comparison of the temperature dependences of magnetization and thermal expansion indicates that magnetic and structural phase

transitions are likely to occur at different temperatures. The similar decoupling of magnetic and structural phase transitions have been observed by neutron diffraction in $Tb_5Si_2Ge_2$ [8]. It also seems to occur in $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ [3] according to magnetization, MCE and magnetostriction data. At first the magnetic ordering occurs in $Gd_{4.95}Ti_{0.05}Si_2Ge_2$ upon cooling. The negative magnetostriction is observed in the vicinity of this phase transition. Then the structural transformation from monoclinic to orthorhombic structure takes place and the positive maximum is observed on $\omega(T)$. In $Gd_5Si_2Ge_2$ the contribution of the structural phase transition is prevailing, therefore the positive magnetostriction is observed. $Gd_{4.9}Ti_{0.1}Si_2Ge_2$ initially crystalizes in orthorhombic structure therefore the structural phase transition is absent in this compound and only the negative magnetostriction due to the orientation of the magnetic moments in magnetic field is observed.

5 Conclusion

With small Ti addition in $Gd_5Si_2Ge_2$, the Curie temperature increases, the thermal hysteresis decreases and the magnetostriction is significantly reduced in magnitude and changes the sign. It is due to the transformation of the magnetostructural phase transition with Ti addition. For $Gd_{4.95}Ti_{0.05}Si_2Ge_2$, the decoupling of magnetic and structural phase transitions is found. At the same time only the magnetic phase transition is observed

in $Gd_{4.9}Ti_{0.1}Si_2Ge_2$ since this compound initially crystalizes in orthorhombic structure.

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