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Magnetocaloric and Magnetoelastic Properties of the $Gd_5Si_2Ge_2$ with Small Indium Substitutions in p-sublattice

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Abstract. The purpose of this work was the complex investigation of magnetic, magnetocaloric and magnetoelastic properties of compounds based on $Gd_5Si_2Ge_2$ with small In substitutions in p-sublattice. The conducted measurements revealed that both the magnetocaloric effect and the volume magnetostriction upon cooling reach the higher values than upon heating. Indium substitution leads to the appearance of the second maximum on the temperature dependence of the magnetocaloric effect resulting in the increase of the refrigerant capacity.

Introduction

The $Gd_5Si_2Ge_2$ compound is known as a material exhibiting the giant magnetocaloric effect and a promising candidate for the magnetic refrigeration [1-3]. Nevertheless most of the results for this compound were obtained by indirect methods. Moreover the influence of thermal and magnetic hysteresis associated with the first order phase transition has not been studied yet.

In this work we present the results of magnetic, magnetocaloric, thermal expansion and magnetostriction measurements of compounds based on $Gd_5Si_2Ge_2$ with small In substitutions in p-sublattice. Particular attention was given to the study of these compounds under the action of high magnetic fields, as well as the study of the thermomagnetic hysteresis. The magnetocaloric effect (MCE) was measured directly and calculated from the magnetization measurements both in pulsed and static magnetic fields.

Experimental details and results

The $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ (2x = 0, 0.05, 0.07, 0.1, 0.15, 0.2) 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 1070 K for 150 h in an argon atmosphere and quenched in ice-cold water. The quality of the samples was evaluated using X-ray diffraction and X-ray spectral microprobe analysis.

X-ray diffraction revealed that the main phase in all compounds is monoclinic $Gd_5Si_2Ge_2$-type phase (space group $P112_1$ / b). In addition to it, there is a small amount of impurity phase in the samples: either the orthorhombic GdGe-type, or hexagonal Gd_5Si_3-type. With increasing of In content the lattice parameters of main phase also increase leading to expansion of the unit cell.

The field and temperature dependencies of magnetization σ were measured in applied magnetic fields up to 12 kOe in the temperature range 80–340 K both upon heating and cooling. The field dependencies of magnetization $\sigma(H)$ were also obtained in high static magnetic fields up to 90 kOe and in high pulsed magnetic fields up to 110 kOe (pulse duration 8 ms) in the temperature range 4.2–320 K. For moderate magnetic fields up to 13.5 kOe MCE measurements were carried out by the direct method with T-type thermocouple attached inside the sample. The sample unit cell unit covered by thermoinsulator was placed in high-vacuum chamber ~ 10^{-4} mm Hg to achieve adiabatic conditions. For high magnetic fields the MCE was calculated using the method based on the compa-

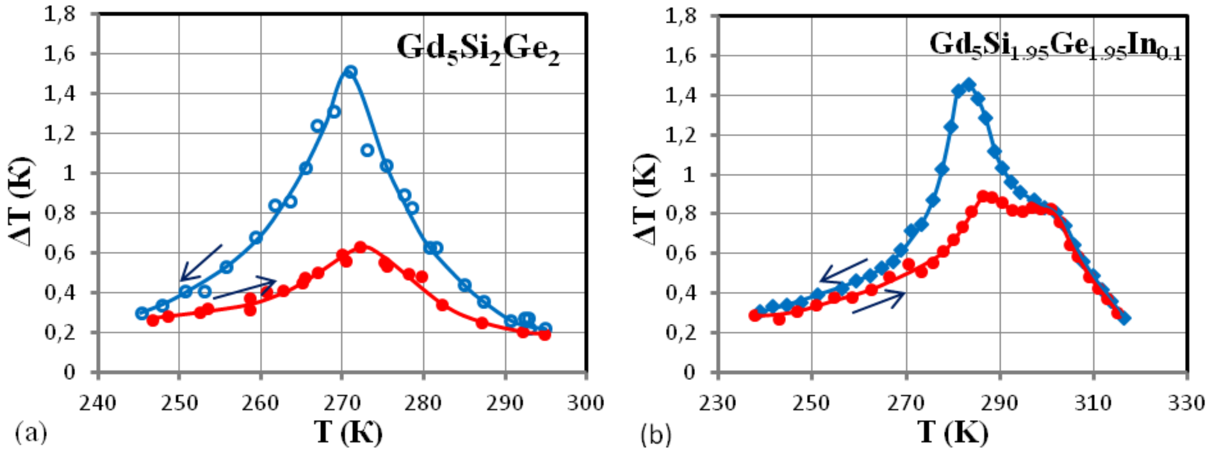

Fig.1. The temperature dependence of MCE in $Gd_5Si_2Ge_2$ *(a) and* $Gd_5Si_{1.95}Ge_{1.95}In_{0.1}$ *(b) for* $\Delta H = 13.5$ *kOe*

rison of magnetization curves obtained in pulsed and static magnetic fields [4]. The magnetic entropy change was calculated from the magnetization isotherms using the well-known Maxwell's relation [3]. 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.

According to the temperature dependencies of magnetization all $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ compounds demonstrate the ferromagnetic behavior. In addition they exhibit the large thermal hysteresis of more than 10 K.

The large thermal hysteresis is also observed on the direct MCE measurements. The $\Delta T(T)$ dependencies upon cooling of the sample have the higher maximal values than upon heating (Fig. 1). Moreover the MCE significantly decreases during the thermocycling. The addition of indium slightly increases both the Curie temperature T_C and the MCE value (Table 1). For 2x = 0.1

Table 1. The magnetic, magnetocaloric and magnetoelastic properties of $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ *compounds from the measurements in the moderate fields.* T_S *and* T_C *are transition temperatures obtained from the dσ/dT curves,* ΔT_{max1} *and* ΔT_{max2} *are the maximal values of the MCE for* $\Delta H = 13.5$ *kOe,* T'_C *is the transition temperature obtained from the thermal expansion measurements,* λ_S *is the largest value of spontaneous magnetostriction,* ω_{max1} *and* ω_{max2} *are the maximal values of the volume magnetostriction in the field of 11.8 kOe.*

alloy	Magnetic measurements		MCE measurements		Thermal expansion and magnetostriction measurements			
	T_S [K]	T_C [K]	ΔT_{max1} [K]	ΔT_{max2} [K]	T'_C [K]	λ_S	ω_{max1}	ω_{max2}
2x=0 on cooling		271	1.5 at 271 K		265	$1.5 \cdot 10^{-3}$	$0.9 \cdot 10^{-3}$ at 270 K	
2x=0 on heating		288	0.6 at 272 K		276	$1.5 \cdot 10^{-3}$	$0.25 \cdot 10^{-3}$ at 276 K	
2x=0.05 on cooling		270.5	1.75 at 275 K		268	$0.55 \cdot 10^{-3}$	$0.4 \cdot 10^{-3}$ at 274 K	
2x=0.05 on heating		290	0.8 at 281 K		280	$0.55 \cdot 10^{-3}$	$0.1 \cdot 10^{-3}$ at 281 K	
2x=0.1 on cooling	278	298	1.5 at 283 K	0.85 at 300 K			$0.14 \cdot 10^{-3}$ at 270 K	$0.07 \cdot 10^{-3}$ at 300 K
2x=0.1 on heating	296	305	0.9 at 286 K	0.85 at 300 K			$0.13 \cdot 10^{-3}$ at 275 K	$0.08 \cdot 10^{-3}$ at 300 K
2x=0.15 on cooling	270	290	1.75 at 284 K	0.95 at 300 K				
2x=0.15 on heating	283.5	298	1.15 at 288 K	0.95 at 300 K				

and 0.15 $\Delta T(T)$ curves have two maxima which are likely to correspond to structural (at T_S) and magnetic (at T_C) phase transitions. Two peaks were also observed on the $d\sigma/dT$ curves for these compounds.

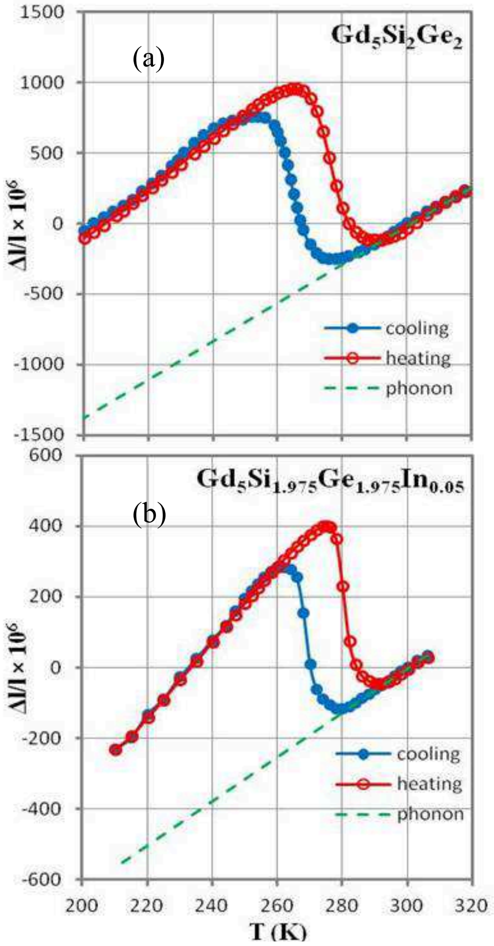

Fig.2. The linear thermal expansion in $Gd_5Si_2Ge_2$ *(a) and* $Gd_5Si_{1.975}Ge_{1.975}In_{0.05}$ *(b)*

The $\sigma(H)$ measurements in high static and pulsed magnetic fields revealed that in the investigated compounds the field-induced phase transition occurs. This phase transition is accompanied by the large magnetic hysteresis. Comparison of magnetization curves measured at the same temperatures in pulsed and static magnetic fields showed that the magnetization measured in pulsed fields is lower than that measured in static fields. It can be associated with the different thermal regimes for measurements in pulsed and static fields. In the pulsed fields the measurements were carried out so rapidly that the magnetization process could be considered as the adiabatic one. At the same time in the case of static fields the constant temperature was kept during the measurements, i.e. the measurements were performed under isothermal conditions.

The ΔT-effect for high ΔH up to 80 kOe was calculated using the comparison of magnetization curves measured under adiabatic and isothermal conditions [4]. In $Gd_5Si_2Ge_2$ compound the maximum ΔT = 13 K for ΔH = 50 kOe was obtained at 270 K which is in a fair agreement with the literature data [1,2].

The magnetic entropy change for investigated compounds was calculated from the $\sigma(H)$ curves. For $Gd_5Si_2Ge_2$ the maximum value of $-\Delta S_M$ was found to be 18.5 J/kg K for ΔH = 50 kOe at 276 K. It is in a good agreement with previously reported data [1]. For In-substituted compounds the maximum value of magnetic entropy change is lower in magnitude compared to the $Gd_5Si_2Ge_2$ compound and occurs at higher temperatures. For example in $Gd_5Si_{1.95}Ge_{1.95}In_{0.1}$ $-\Delta S_M$ reaches 13.5 J/kg K for a field change of 50 kOe at 285 K.

The high values of the MCE in the $Gd_5Si_2Ge_2$ based compounds are usually associated to the presence of the magnetic phase transition accompanied by a structural transformation [2]. Therefore the thermal expansion and magnetostriction measurements were carried out to get more information about the processes occurring in investigated compounds.

The linear thermal expansion measurements like the magnetic ones revealed that $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ compounds exhibit large thermal hysteresis (Fig.2) and Curie temperature increases with In substitution. However the T_C values obtained from the thermal expansion data are lower than those determined from the $d\sigma/dT$ curves. It can be related to the fact that unlike the magnetization the thermal expansion was measured in the absence of the magnetic field.

The spontaneous magnetostriction λ_S was calculated by subtracting the phonon contribution from the linear thermal expansion. For $Gd_5Si_2Ge_2$ λ_S reaches $1.5{\cdot}10^{-3}$ at 240 K whereas in $Gd_5Si_{1.975}Ge_{1.975}In_{0.05}$ it doesn't exceed the value of $0.6{\cdot}10^{-3}$, i.e. spontaneous magnetostriction decreases with In substitution.

For $Gd_5Si_{2-x}Ge_{2-x}In_{2x}$ (2x = 0, 0.05, 0.1) compounds the temperature dependences of volume magnetostriction $\omega(T)$ in the magnetic field of 11.8 kOe was also obtained. Like the ΔT the volume magnetostriction is larger if the measurements are carried out upon cooling (Fig. 3). In addition for

$Gd_5Si_{1.95}Ge_{1.95}In_{0.1}$ compound ω(*T*) curves have two maxima. The increase in In content leads to the decrease of volume magnetostriction (Table 1).

Discussion

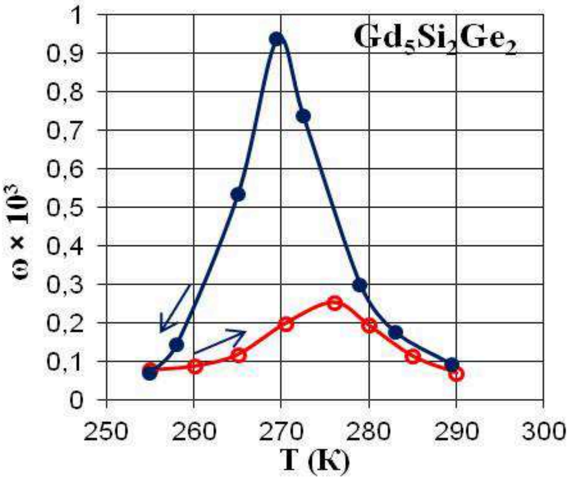

Fig.3. The temperature dependence of volume magnetostriction for $Gd_5Si_2Ge_2$ in the magnetic field of 11.8 kOe

Our MCE measurements revealed that MCE values obtained upon heating of the sample is significantly lower compared to that observed upon cooling. Moreover MCE decreases markedly during the thermocycling. Probably it is associated to the irreversible effects in magnetostructural first order phase transitions. Mentioned two features lead to limitations in practical use of the investigated compounds.

Indium substitution leads to the appearance of the second maximum on the temperature dependence of MCE resulting in the increase of the refrigerant capacity. This effect may be related to the decoupling of magnetic and structural phase transitions, which occurs when the lattice expands with In substitution. Similar behavior takes place for $Tb_5Si_2Ge_2$ compound, in which according to the neutron diffraction study it was found that structural and magnetic phase transitions occur at different temperatures ($T_S \approx 93$ K, $T_C \approx 111$ K) [5]. In the work [6] it was shown that under the action of the hydrostatic pressure in $Tb_5Si_2Ge_2$ compound these phase transitions can be coupled.

Summary

The indirect methods of MCE investigation used in this work yield the results which are in good agreement with literature data for $Gd_5Si_2Ge_2$ compound. The direct measurements revealed that the maximal MCE and magnetostriction values are varies greatly upon cooling and upon heating. Indium substitution was found to result in the appearance of the second maximum on the temperature dependence of MCE. This effect seems to be associated with the decoupling of the magnetic and structural transitions.

Acknowledgments

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