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Properties of the GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$ intermetallics

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ABSTRACT

The magnetic and magnetocaloric properties of GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$ ternary compounds for possible applications in magnetic refrigeration have been investigated. Magnetization measurements have been performed in the temperature range of 2–400 K and magnetic field range of 0–7 T. The magnetic entropy changes ΔS_m have been calculated indirectly from the magnetization measurements. The calculated values of entropy change ΔS_m for examined compounds amount −13.63 J/K kg, −13.05 J/K kg, −6.13 J/K kg, −3.72 J/K kg, −1.38 J/K kg and −0.94 J/K kg, respectively, for GdNiAl, GdPdAl, GdPdIn, GdFeAl, $GdFe_6Al_6$ and GdMnAl at 7 T.

1. Introduction

The intermetallic ternary compounds of the RTX type, consisting of the rare earth *R*, transition metal *T* and the *p* element *X*, exhibit an enormously rich variety of crystallographic structures and magnetic properties. Some of these compounds could exist in various crystallographic structures. The well known example is GdPdAl (TiNiSi or ZrNiAl) [1]. The physical properties of the GdCoAl, GdNiAl, GdCuAl, GdRhAl and GdPdAl depend on the history of the sample [2]. The RPdAl annealed samples obtained by Dwight crystallized in the orthorhombic TiNiSi structure, while the rapidly cooled samples turned out to be hexagonal ZrNiAl as reported by Hulliger [3,4]. Moreover, for the GdPdAl and GdNiAl the isostructural phase transition from the high temperature phase modification HTM I to the low temperature phase modification HTM II take place [5,6].

Recently, it has been pointed out that the use of magnetic materials with relatively high magnetic transition temperatures may be used in magnetic refrigeration cycles. It is expected that magnetic refrigeration in several years will be available for consumers as a more efficient and more environmentally safe alternative to conventional type refrigerators. The discovery of new magnetocaloric materials with relatively high Curie temperatures (T_C), and large magnetocaloric effects (MCE) has giant value for magnetic refrigeration. Recent measurements of $Gd_5(Ge_{1-x}Si_x)_4$ [7,8], $MnFe(P_{1-x}As_x)$, $Mn(As_{1-x}Sb_x)$ and also $La(Fe_{13-x}Si_x)$ [9,10] reveal a considerable magnetocaloric effect (MCE). It is believed that the use of a new class of materials based on gadolinium will eventually end in the production of such magnetic refrigerators. The main aim of this work was to enlarge the examinations of the magnetic properties and calculate a magnetocaloric effect of polycrystalline samples of intermetallic compounds GdTX (T = metal 3d, 4d, 5d; X = metal sp) and $GdFe_6Al_6$. The calculations of the magnetic entropy change, ΔS_m, were performed using the isothermal magnetization curves.

2. Experimental

The polycrystalline samples were prepared by induction melting of the pure constituents in stoichiometric amounts. The samples were remelted several times in order to ensure complete homogenisation.

Crystalline phase identification was carried out by power X-ray diffraction with Cu (K_α) radiation using a Siemens D-5000 diffractometer.

Magnetic measurements were conducted using a Quantum Design MPMS-XL-7AC SQUID magnetometer. Magnetization of the samples was measured in the temperature range 2–300 or 400 K and magnetic fields up to 7 T.

3. Results and discussion

From the powder X-ray diffraction pattern the ZrNiAl-type crystal structure was confirmed for GdNiAl, GdPdAl and GdPdIn compounds, $MgZn_2$-type structure was confirmed for GdFeAl, $ThMn_{12}$-type structure for $GdFe_6Al_6$ and for GdMnAl the cubic $MgCu_2$-type structure was confirmed. The determined lattice constants were in good agreement with the data reported previously [5,11–15]. The lattice parameters for the investigated compounds are collected in Table 1.

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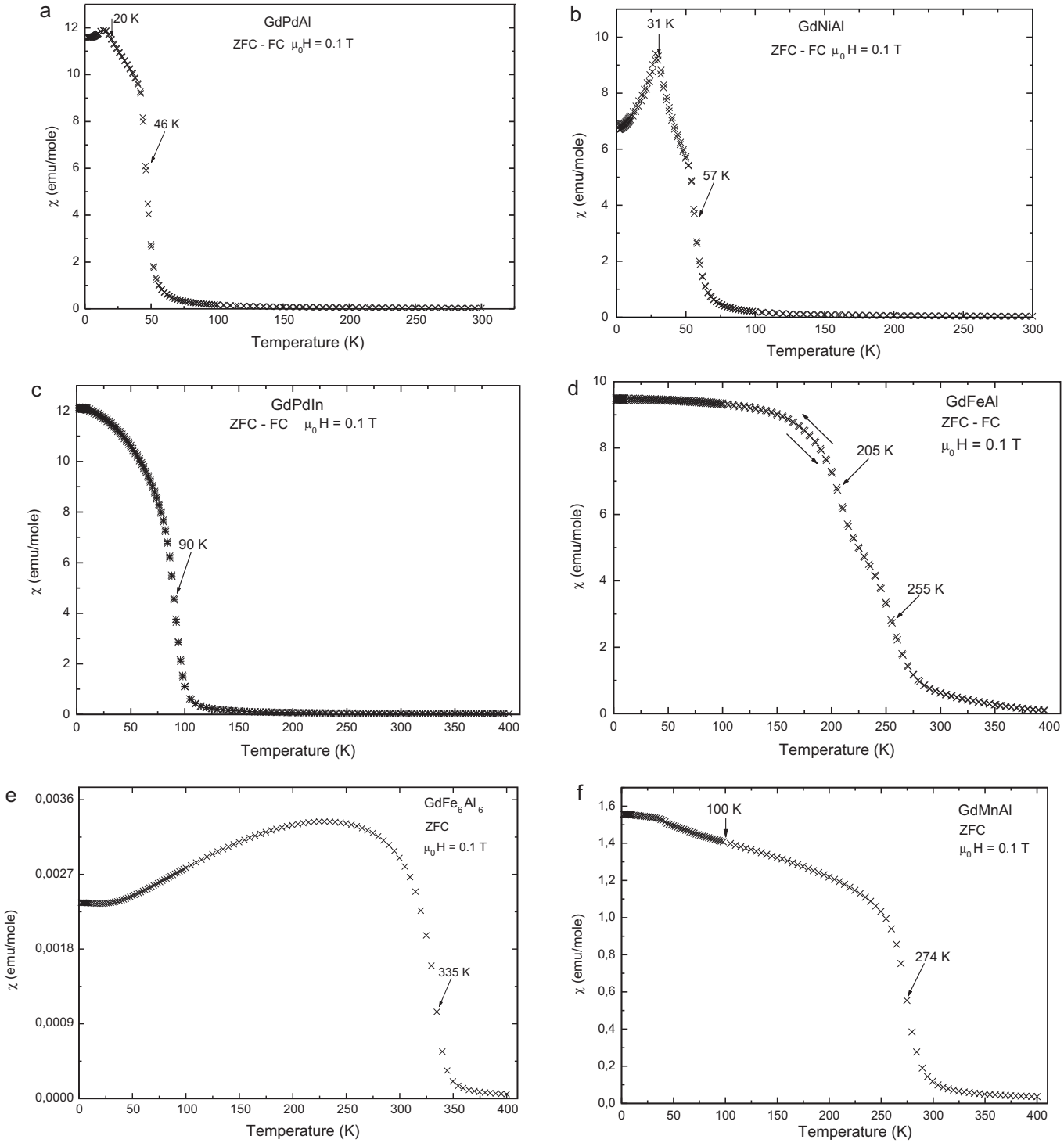

Fig. 1. The *dc* magnetic susceptibility under a magnetic field of 0.1 T for (a) GdPdAl, (b) GdNiAl, (c) GdPdIn, (d) GdFeAl, (e) $GdFe_6Al_6$, (f) GdMnAl.

The measurements of *dc* magnetic susceptibility show that the GdPdAl exhibits two magnetic transitions at 46 and 20 K, respectively (Fig. 1a). The obtained transition temperatures and the shape of the curves are consistent with the report in Ref. [5].

For the GdNiAl the magnetic phase transition at $T_C = 57$ K and additional transition at $T_1 = 31$ K is observed (Fig. 1b). This value of the Curie temperature is in agreement with that reported in Ref. [16]. The second transition at T_1 may be attributed to the antiferromagnetic arrangement of the magnetic moments. Moreover, in *ac* magnetic susceptibility measurements an additional transition at 8 K is visible (Fig. 2b). Previously, for the GdNiAl compound the existence of the additional transitions has been found [11].

The GdPdIn orders ferromagnetically at $T_C = 90$ K (Fig. 1c). The obtained Curie temperature is lower than that in Ref. [17], but the shape of the curve is similar.

Fig. 1d shows the *dc* magnetic susceptibility $M(T)$ curve of GdFeAl compound. A magnetic phase transition takes place at Curie temperature $T_C = 250$ K (Fig. 1d). Besides the magnetic phase transition at 250 K, defined as the minimum in the temperature derivative of the magnetization dM(T)/dT, we detect an anomaly around

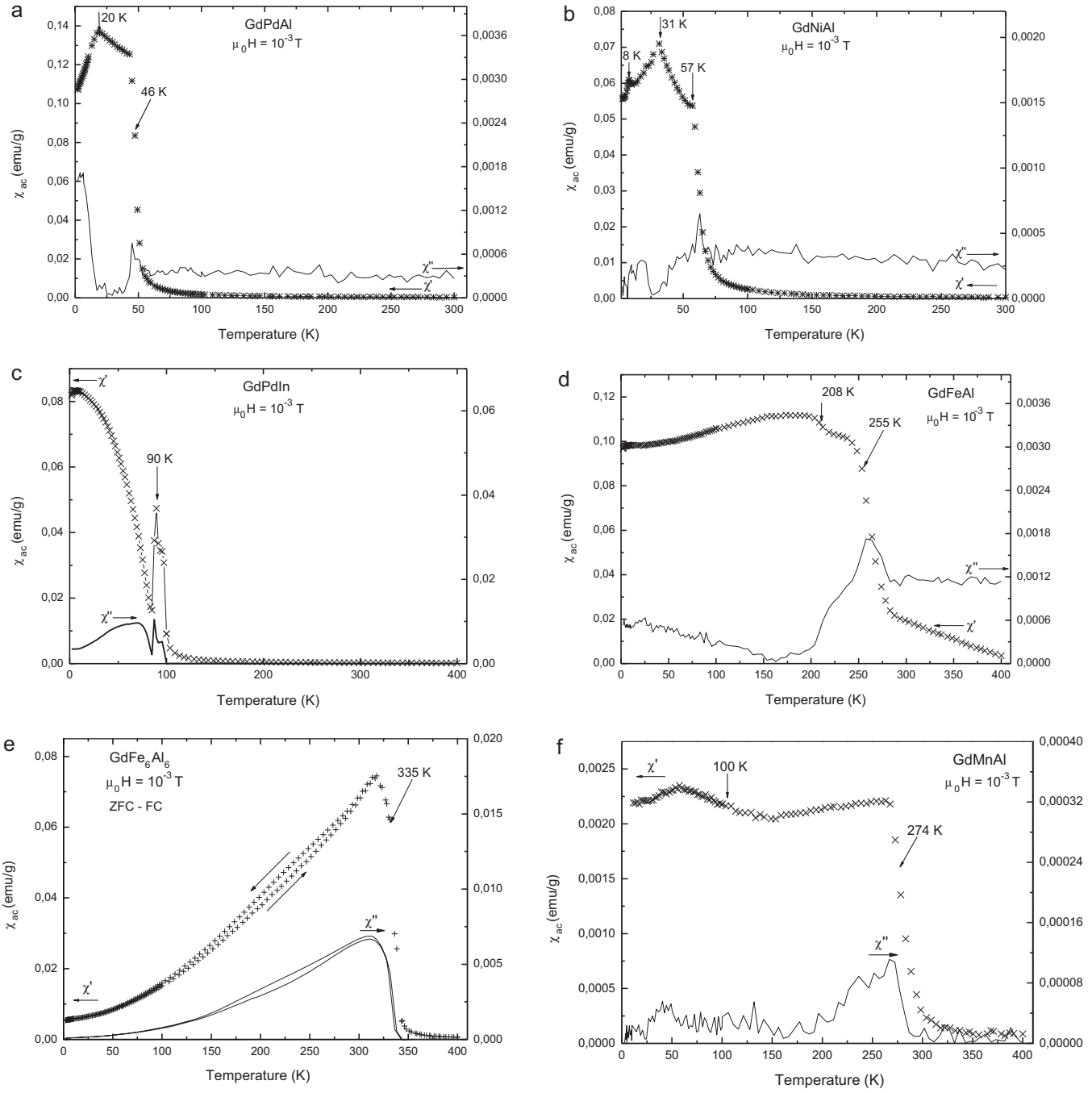

Fig. 2. The *ac* magnetic susceptibility for (a) GdPdAl, (b) GdNiAl, (c) GdPdIn, (d) GdFeAl, (e) $GdFe_6Al_6$, (f) GdMnAl.

210 K. Dong et al. [18] attributed this behaviour to the existence of the small impurity in the sample.

The determined Curie temperature of the $GdFe_6Al_6$ (T_C = 334 K) (Fig. 1e) is lower than that obtained by Duong et al. [19].

The GdMnAl exhibits magnetic transition at 274 K (Fig. 1f). Moreover, for this compound we detect an anomaly below 100 K. We tentatively interpret this anomaly as due to some reorientation of the Gd-spins. The determined value of the transition temperature is lower than obtained by Chevalier et al. [15] (T_1 = 298 K) and higher than that reported in Ref. [20] (≅202 K). The observed anomalies below 100 K is also visible in the $\Delta S_m(T)$ curve as the second peak.

The transitions visible in the *dc*-magnetization measurements are confirmed by the real *ac*-susceptibility data (Fig. 2a–f). The peaks in the imaginary part are connected with energy dissipation during the reorientation process.

The calculations of the magnetic entropy change, ΔS_m, were performed using the isothermal magnetization curves. To determine ΔS_m from magnetization measurements following equation was used:

$$\Delta S_m = \sum_i \frac{M(T_{i+1}, H) - M(T_i, H)}{T_{i+1} - T_i} \Delta H$$

where $M(T_i, H)$ and $M(T_{i+1}, H)$ represent the value of the magnetization at a temperature T_i and T_{i+1} respectively, under magnetic field intensity of H; and ΔS_m is the magnetic entropy change.

Table 1
The lattice parameters of GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$.

Parameters		Crystal structure	References
a [Å]	*c* [Å]		
GdNiAl			
7.019	3.916	ZrNiAl	This work (300 K)
GdPdAl			
7.1951	4.0353	ZrNiAl	This work (300 K)
GdPdIn			
7.647	3.887	ZrNiAl	This work (300 K)
GdFeAl			
5.442 1(6)	8.831	$MgZn_2$	This work (300 K)
$GdFe_6Al_6$			
8.6747	5.0368	$ThMn_{12}$	This work (300 K)
GdMnAl			
7.875	–	$MgCu_2$	This work (300 K)

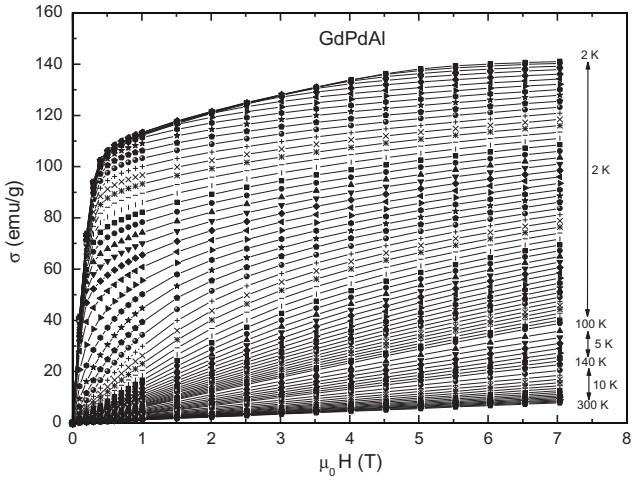

Fig. 3. The isotherm magnetization curves for GdPdAl.

Some example data of the isotherm magnetization curves for GdPdAl are shown in Fig. 3. Fig. 4 presents the temperature dependence of the entropy change for different magnetic field variations for GdPdAl [21]. The maximum value of the entropy change is located at a temperature near the magnetic transition temperature of the GdPdAl, (T_C = 46 K). The maximum entropy change value obtained at 3, 5 and 7 T amounts −5.57 J/K kg, −10.41 J/K kg and −13.05 J/K kg, respectively. For the GdNiAl the maximum entropy change value obtained at 3, 5 and 7 T amounts −7.19 J/K kg, −10.6 J/K kg and −13.63 J/K kg, respectively. The calculated values of the ΔS_m were in good agreement with the data reported in Refs. [22,23]. The value of the magnetic entropy change for the GdFeAl is comparable with published by Dong et al. [18].

The results of the calculated magnetic entropy changes, ΔS_m, for all other investigated compounds are shown in Figs. 5a–e [21]. The maximal values of magnetocaloric effect at the temperatures near the magnetic transition temperatures for investigated compounds are observed.

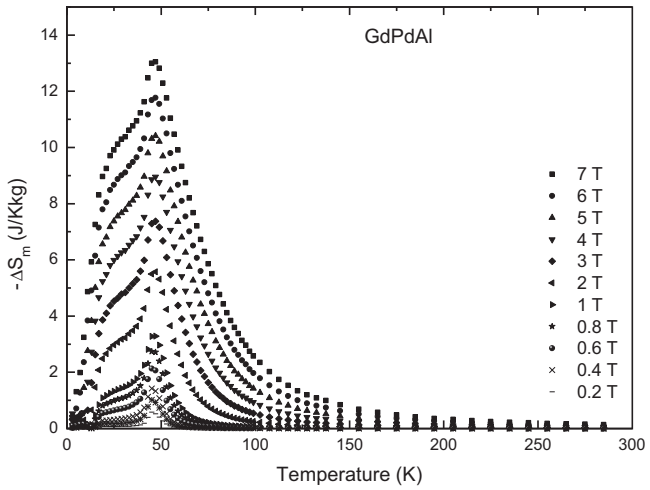

Fig. 4. The temperature dependence of the entropy change for different magnetic field variations for GdPdAl.

Fig. 6 presents the calculated entropy change for above compounds at magnetic field of 5 T. This comparison shows the differences between the values of MCE and the shapes of curves for each compound.

The field dependence of the $\Delta S_m{}^{max}$ for all investigated compounds is shown in Fig. 7. For two compounds: GdNiAl and GdPdAl the highest values of the magnetic entropy change is observed. For the both compounds the isostructural phase transition from the high temperature phase modification HTM I to the low temperature phase modification HTM II take place [5,6]. Therefore, the large magnetocaloric effect may be connected with isostructural transitions.

A comparison of the values of magnetic entropy change for all polycrystalline compounds is collected in Table 2. Moreover, for all investigated compounds the RC (refrigerant capacity) was calculated (Table 2). The RC values were determined by numerically integrating the area under the $\Delta S_m(T)$ curve, using the temperatures at half maximum of the ΔS_m peak as the integration limits:

$$RC = \int_{T_1}^{T_2} \Delta S_m(T) dT.$$

Fig. 8 shows the field dependence of RC for all investigated compounds for a field change of 0–7 T. The values of RC for all compounds are lower than that of pure Gd (556 J/kg). However, the values of RC for GdNiAl, GdPdAl, GdPdIn, GdFeAl are much higher than those of $Gd_5Si_2Ge_2$ (305 J/kg) [18] (Table 2). The value of RC for GdFeAl compound is 438 J/kg for a field change of 0–5 T. This value is comparable with that reported in Ref. [18].

Next important for refrigeration parameter is the relative cooling power (RCP) as a measure of the amount of transferred heat,

Table 2
The comparison of magnetic entropy change $|\Delta S_m|$ for GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$.

Compound	Transition temperature (K)	Γ_{FWHM} [K]	RC 0–5 T [J/kg]	$\|\Delta S_m\|$ [J/K kg]		
				2 T	5 T	7 T
GdNiAl	57	52	460	5.17	10.6	13.63
GdPdAl	46	54	422	5.57	10.41	13.05
GdPdIn	90	100	375	2.08	4.64	6.13
GdFeAl	200	205	438	1.22	2.78	3.72
$GdFe_6Al_6$	334	61	53	0.56	1.1	1.38
GdMnAl	274	86	39	0.31	0.69	0.94

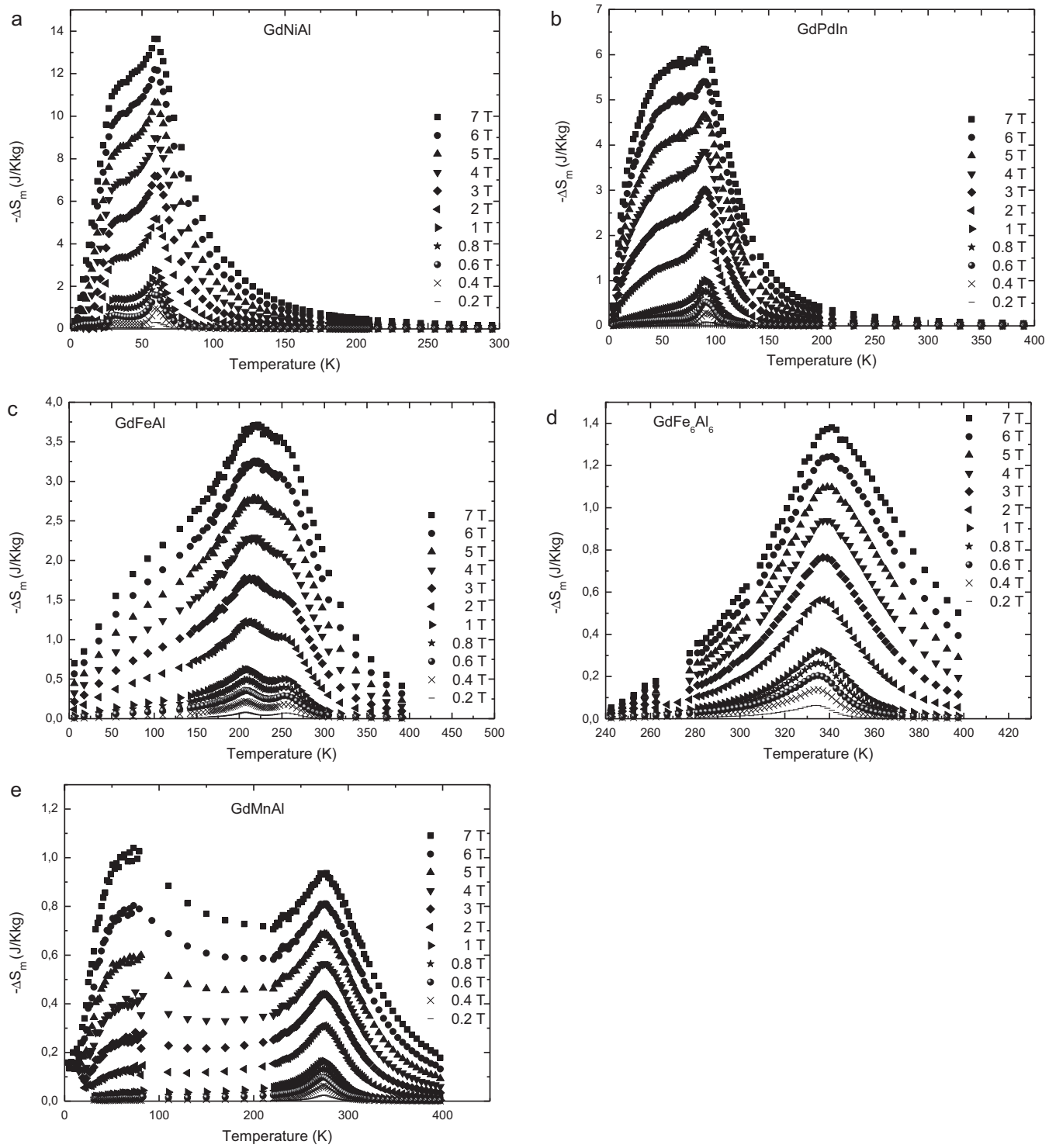

Fig. 5. Calculated entropy change for different magnetic field variations for (a) GdNiAl, (b) GdPdIn, (c) GdFeAl, (d) $GdFe_6Al_6$, (e) GdMnAl.

Table 3
The magnetocaloric properties of GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$.

Compound	$-\Delta S_m{}^{max}$ (7 T) (J/kg K)	RCP (7 T) (J/kg)	$-\Delta S_m{}^{max}$ (5 T) (J/kg K)	RCP (5 T) (J/kg)	$-\Delta S_m{}^{max}$ (2 T) (J/kg K)	RCP (2 T) (J/kg)
GdNiAl	13.63	~845	10.6	~551	5.17	~207
GdPdAl	13.05	~731	10.41	~562	5.57	~200
GdPdIn	6.13	~637	4.64	~464	2.08	~154
GdFeAl	3.72	~855	2.78	~570	1.22	~210
$GdFe_6Al_6$	1.38	~101	1.1	~65	0.56	~25
GdMnAl	0.94	~81	0.69	~59	0.31	~25

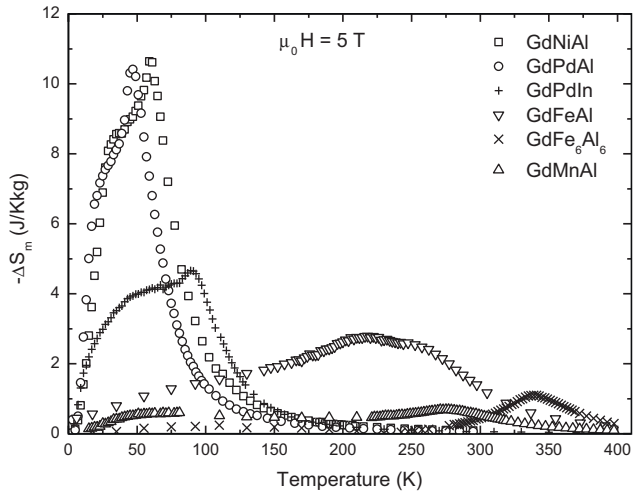

Fig. 6. The calculated maximum entropy change, $\Delta S_m{}^{max}$, for all investigated compounds at magnetic field of 5 T.

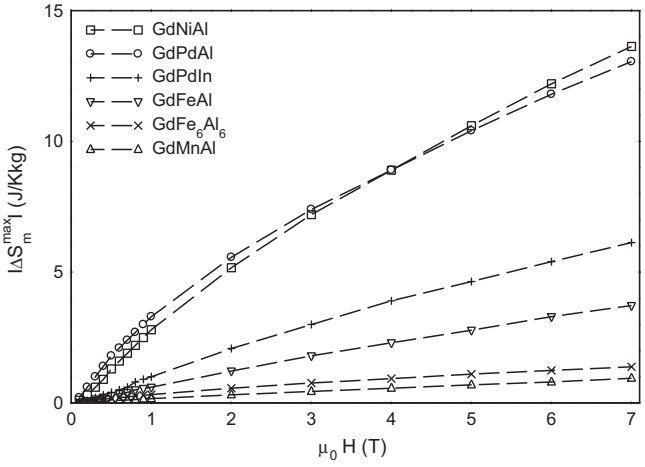

Fig. 7. Field dependence of the $\Delta S_m{}^{max}$ for GdPdAl, GdNiAl, GdPdIn, GdFeAl, $GdFe_6Al_6$ and GdMnAl.

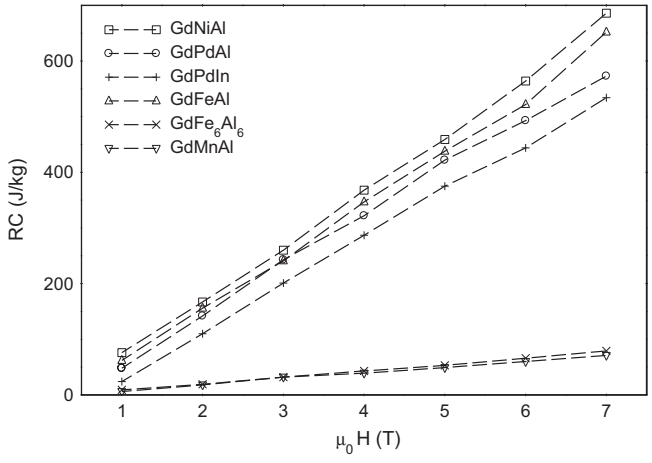

Fig. 8. Field dependence of RC for GdPdAl, GdNiAl, GdPdIn, GdFeAl, $GdFe_6Al_6$ and GdMnAl.

which can be calculated using a formula:

$$\mathrm{RCP}(S) = -\Delta S_m^{\max} \delta T_{\mathrm{FWHM}},$$

where δT_{FWHM} is the full width at half maximum of the $\Delta S_m(T)$ curve [24] (Table 3).

According to Gschneidner and Pecharsky [25] RCP(S) gives a value close to 4/3 times the refrigerant capacity (RC) discussed above in the same temperature range. For the investigated compounds the obtained values of *RCP* are in agreement with this rule. The determined RCP values are again smaller than that of pure Gd [26] but for GdNiAl, GdPdAl, GdPdIn, GdFeAl compounds exhibit much higher than those of $Gd_5Si_2Ge_2$ [26].

In conclusion, the investigations of the magnetocaloric effect in GdTX (T = Mn, Fe, Ni, Pd, X = Al, In) and $GdFe_6Al_6$ were presented. The highest value of MCE for GdNiAl under the magnetic field changes 0–5 T and 0–7 T was found. The detailed investigations of the other compounds reveal lower values of MCE. For all investigated compounds the peak value of the entropy change, ΔS_m, is located near the magnetic temperature transition of the magnetic material. The GdNiAl, GdPdAl and GdPdIn display interesting properties but for magnetic refrigerant working in near room temperature range their transition temperatures are too lower. The GdFeAl, $GdFe_6Al_6$ and GdMnAl exhibit ordering temperature near room temperature, no hysteresis loss and the half-height width of the MCE peaks are large enough in order that be used as an active magnetic refrigerator in a wide range of the temperature. Unfortunately low values of the entropy change are the disadvantages of these compounds.

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