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Magnetism of selected ternary Sm compounds

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ABSTRACT

The effect of In for Sn and Gd for Sm substitution on magnetic properties of the $SmPdSn_{1-x}In_x$ and $Gd_xSm_{1-x}PdIn$ compounds has been studied. The behaviour of the first series differs markedly from the second one. One of the most visible difference in the magnetic properties is the fact, that in the $SmPdSn_{1-x}In_x$ series the so called non-Curie–Weiss (NCW) behaviour is observed whereas in the case of the gadolinium series the Curie–Weiss law (CW) is fulfilled. The values of magnetic phase transition temperatures, magnetic moment obtained at 7 T and magnetocaloric effect are much higher for Gd-rich compounds.

1. Introduction

The ternary RPdSn or RPdIn (where R is a rare earth element) compounds have been intensively investigated in the past with respect to their crystal structure, magnetic and transport properties [1–5] that generally are ruled by the f–d interactions. However, in the compounds with the hexagonal type of crystal structure some properties are connected with a frustration in R sublattice. Such interesting mechanism can lead to an existence of the mixed valence, heavy fermion or Kondo effect.

The first group of compounds RPdSn (where R = Ce–Dy) crystallize in the orthorhombic TiNiSi type of crystal structure (*Pnma* space group) whereas with R = Er–Sc crystallize in the hexagonal Fe_2P structure (*P-62m* space group). The HoPdSn compound can exist in the both structures which depends on a heat treatment [1,3]. It was already observed that the RPdSn group of intermetallic compounds with R = Ce–Er is ordered antiferromagnetically. The Neel temperature is ranging from 7.5 K for Ce up to 23.5 K for Tb. The compounds with R = Pr–Tm are paramagnetic in the whole range of temperatures down to 4.2 K. Very interesting are the two compounds EuPdSn and YbPdSn. For both of them it was shown that the volume of the unit cell as a function of R ion content exhibits the deviation from the linear dependence. It means that Eu and Yb ions in these compounds are not in trivalence state but may occur in the divalence state or in a mixed valence state [1]. The susceptibility of the policrystalline SmPdSn compound deviates form Curie–Weiss behavoiur. As it was previously reported this compound exhibits antiferromagnetic ordering with T_N about 12 K. However, in low temperature range there was observed additional peak which is probably connected with more complex magnetic structure [1,3].

The second group of compounds RPdIn (R = La–Sm,Y, Gd–Lu) with 4d elements crystallize in the ZrNiAl – type hexagonal structure (*P-62m* space group) [2,4,5]. The most known compound from this group is GdPdIn which exhibits ferromagnetic phase transition at $T_C = 102$ K and Curie–Weiss behaviour with the paramagnetic Curie temperature $\theta_p = 96.5$ K [2]. The compounds with Td and Dy are ferrimagnetically ordered below 66 K and 31 K, respectively. The SmPdIn single crystal is a ferromagnet below 54 K and the magnetic moment is 0.21 μ_B/Sm along the easy magnetization *a*-axis [4]. The lowest temperatures of magnetic phase transition was already found for HoPdIn and ErPdIn where $T_C = 25$ K and 12.3 K, respectively [2].

In this paper we are focused on the influence of indium and gadolinium substitution on the magnetic properties the $SmPdSn_{1-x}In_x$ ($x = 0.0, 0.5, 1.0$) and $Gd_xSm_{1-x}PdIn$ ($x = 0.0, 0.5, 1.0$) compounds.

2. Experimental details

The polycrystalline samples $SmPdSn_{1-x}In_x$ ($x = 0.0, 0.5, 1.0$) and $Gd_xSm_{1-x}PdIn$ ($x = 0.0, 0.5, 1.0$) were prepared by arc-melting from high purity elements under argon atmosphere. The melted samples were then wrapped in tantalum foil, placed in quartz tubes and annealed at 850 °C for 1 week. After annealing all studied samples were single phase and their crystal structure was checked by means of X-ray diffraction (XRD) using the Siemens D5000 diffractometer.

The magnetic properties of examined samples were measured with the use of SQUID magnetometer (MPMS XL7 Quantum Design). Thermal dependence of magnetization $M(T)$ was measured in the 2–400 K temperature range at 0.1 T applied magnetic field. Isothermal magnetization measurements were done at selected temperatures and up to 7 T magnetic field.

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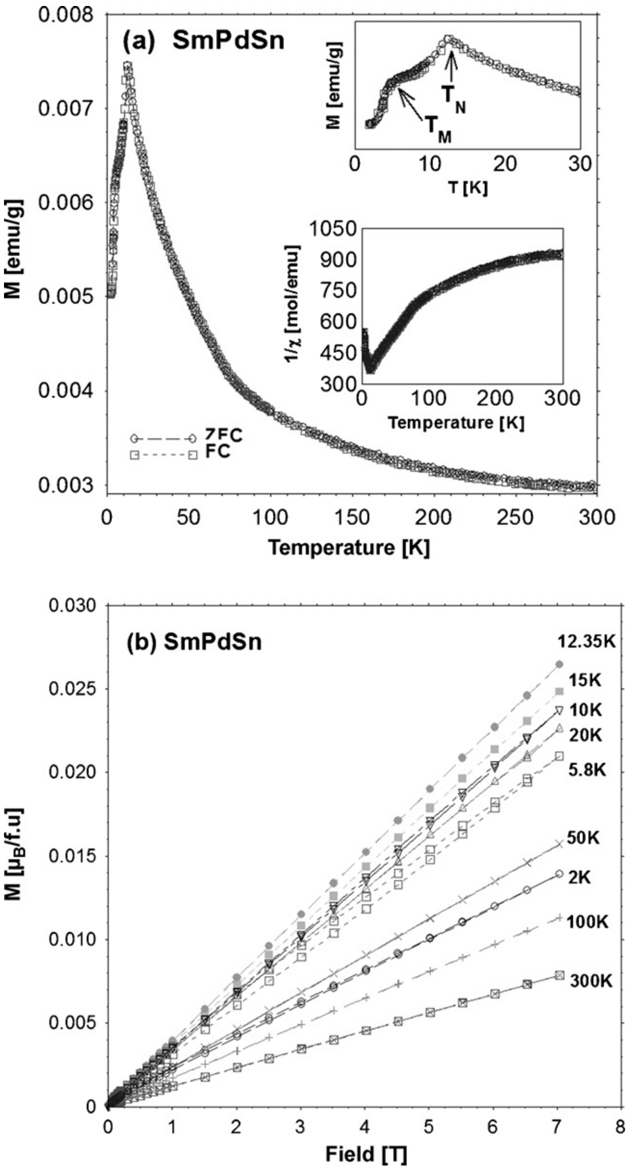

Fig. 1. (a) Temperature variation of magnetization of the SmPdSn compound in 0.1 T. The upper inset shows $M(T)$ in low temperature range. The lower inset represents $1/\chi\,(T)$ dependence. (b) The magnetic isotherms measured in the temperature range 2–300 K up to 7 T for the SmPdSn compound.

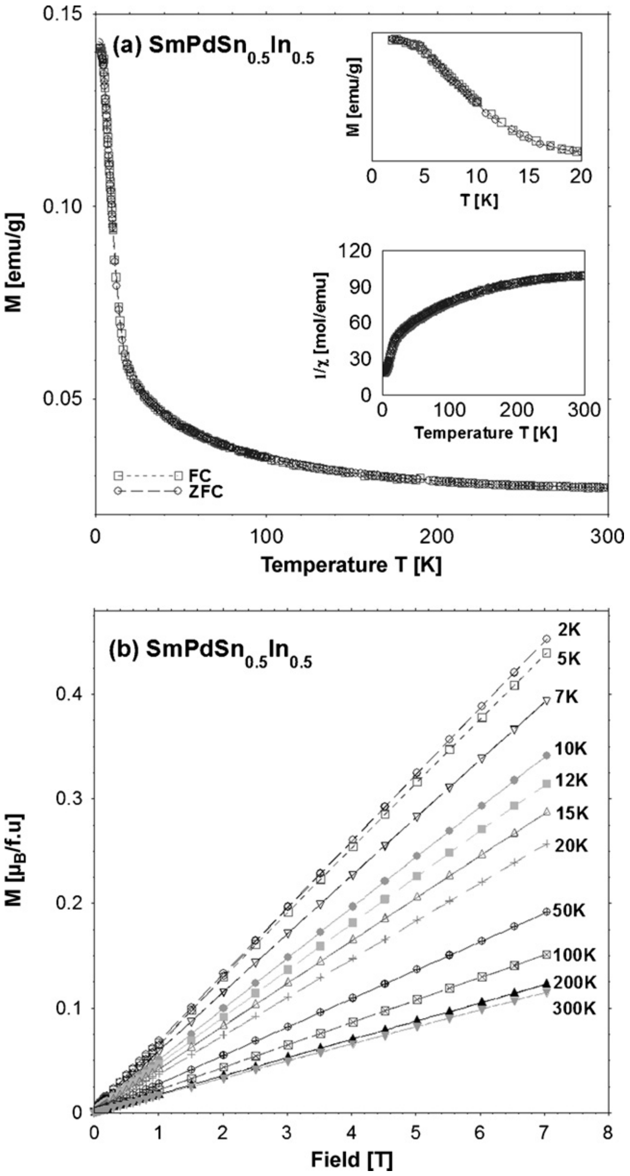

Fig. 2. (a) Temperature variation of magnetization of the $SmPdSn_{0.5}In_{0.5}$ compound in 0.1 T. The upper inset shows $M(T)$ in low temperature range. The lower inset represents $1/\chi\,(T)$ dependence. (b) The magnetic isotherms measured in the temperature range 2–300 K up to 7 T for the $SmPdSn_{0.5}In_{0.5}$ compound.

3. Results and discussion

3.1. Magnetic properties

The temperature dependence of magnetization for all studied compounds was measured in the applied magnetic field 0.1 T. All the measurements were performed in two ways. One curve was obtained when the samples were cooled in zero magnetic field (ZFC) and the second when the samples were cooled in the 0.1 T magnetic field (FC). Fig. 1a depicts such experiment curried out for the SmPdSn compound. The $M(T)$ curve reveals an antiferromagnetic behaviour with the Neel temperature T_N of 12.5 K and a second magnetic transition in the temperature $T_M = 4.5$ K. Fig. 1b presents a family of magnetic isotherms measured in the temperature range from 2 K to 300 K and magnetic field up to 7 T. For all the temperature range the magnetization shows a linear field dependence. In the case of the $SmPdSn_{0.5}In_{0.5}$ a partial substitution of Sn for In causes a significant change of its magnetic properties (see Fig. 2a). As we can see from this figure the magnetization remarkable increases in temperature range about 10 K and than saturates below 5 K. Similarly to the SmPdSn sample the isotherms presented in Fig. 2b exhibit a linear field relation. Further indium substitution (SmPdIn) leads to an appearing of a distinct magnetic phase transition at the temperature of 38 K which is shown in Fig. 3a. This fact is confirmed by a saturation character of the magnetic isotherms obtained below the transition temperature (Fig. 3b). It should be stressed that for all described above cases the $M(T)$ relation do not fulfill the Curie–Weiss low that is proved by the $1/\chi$ curves (see the insets in Figs. 1a, 2a and 3a). Next investigations have concerned effect of Sm substitution for Gd on magnetic properties of the SmPdIn compound. It is shown in Fig. 4a ($M(T)$, $1/\chi$) and in Fig. 4b ($M(H)$) that the $Sm_{0.5}Gd_{0.5}PdIn$ compound magnetically behave as a typical ferromagnet with the Curie temperature $T_C = 60$ K (defined at the maximum of $|dM/dT|$). Similar results were obtained for the GdPdIn compound (Fig. 5) with this reservation that T_C is shifted to 83 K. Taking into account the $1/\chi$ curves (insets

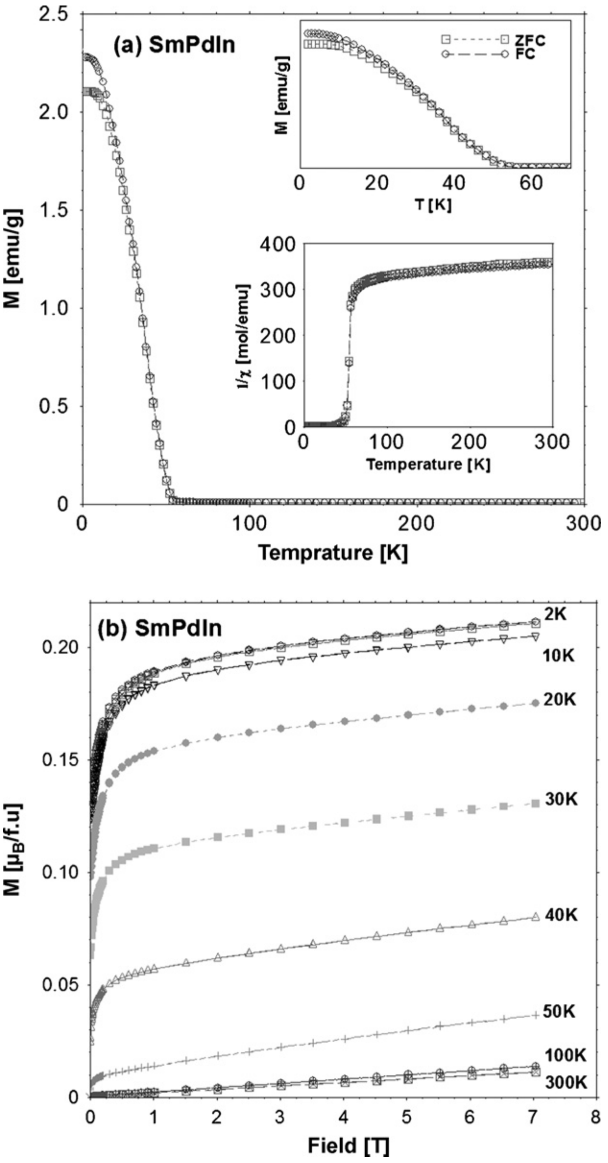

Fig. 3. (a) Temperature variation of magnetization of the SmPdIn compound in 0.1 T. The upper inset shows $M(T)$ in low temperature range. The lower inset represents $1/\chi(T)$ dependence. (b) The magnetic isotherms measured in the temperature range 2–300 K up to 7 T for the SmPdIn compound.

in Figs. 4a and 5a) one can state that the gadolinium rich compounds follow the Curie–Weiss relation.

Generally, for the all sample tested the difference between ZFC and FC curves can be neglect. There are only two exceptions, i.e., the SmPdIn and GdPdIn compounds. This small thermomagnetic irreversibility may be due to the domain wall pinning effect. In the SmPdIn compound it is better visible than in GdPdIn and it is evident that FC–ZFC effect comes from anisotropy due to the R ions. This kind of ZFC–FC behaviour can appear in ferromagnetic systems if the alignment of the magnetic domains is restricted by impediment or barrier energy. The zero field cooling leads to a pinning effect of domain walls. The small applied magnetic field causes alignment of some domains. With the increasing of temperature the barrier energy becomes smaller and it is reflected in the increasing of magnetization.

For all studied compounds at low temperatures the magnetization increases with decreasing temperature. The value of magnetization is much higher for Gd – rich compounds or even in In – rich compounds. It is connected with f–d interactions and some kind of hybridization effect in valence band due to the change of electron number (Sn has one 5p electron more than In, Gd has one 5d electron more and one 4f electron less than Sm^{2+} or two 4f electrons less than Sm^{3+}).

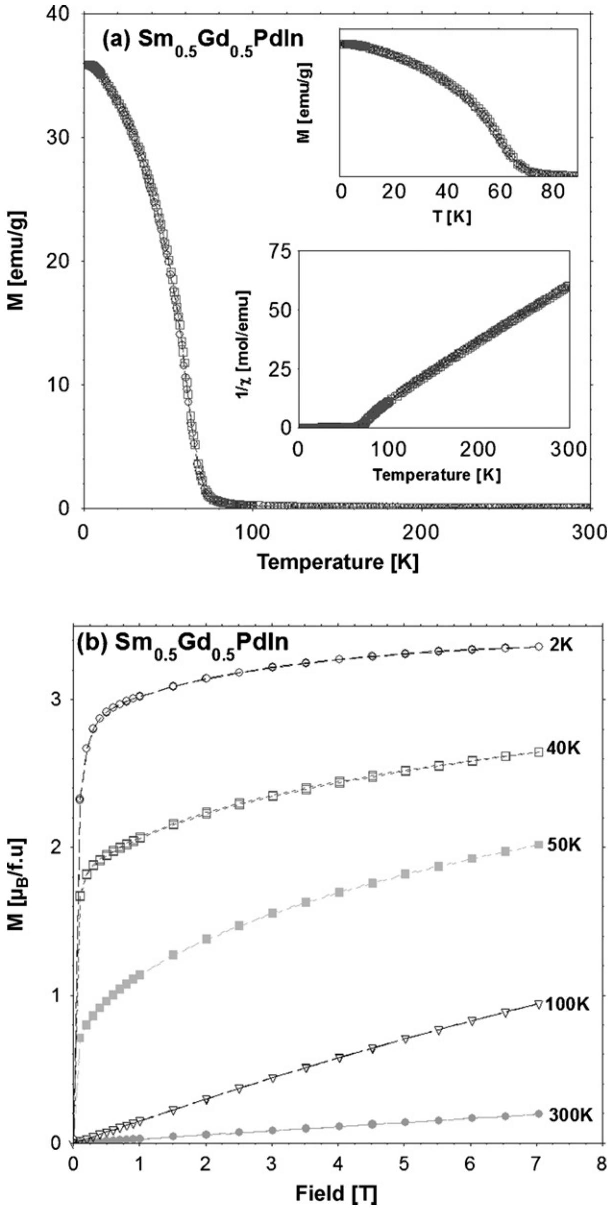

Fig. 4. (a) Temperature variation of magnetization of the $Gd_xSm_{1-x}PdIn$ compound in 0.1 T. The upper inset shows $M(T)$ in low temperature range. The lower inset represents $1/\chi(T)$ dependence. (b) The magnetic isotherms measured in the temperature range 2–300 K up to 7 T for the $Gd_{0.5}Sm_{0.5}PdIn$ compound.

The magnetization of SmPdSn exhibits two kinds. First on them is visible at about $T_M = 4.5$ K, second at about $T_N = 12.5$ K. The first peak is connected with other magnetic transition below T_N. The presence of these two peaks was already observed for the polycrystalline SmPdSn in an association with the specific heat and resistivity measurements [3]. As it was noticed that the origin of the low temperature peak can be connected with quadrupolar ordering, a spin flipping or antiferromagnetic complicated structure.

The substitution of indium atoms in the place of tin causes a change of character and a temperature of magnetic phase transition. For the $SmPdSn_{0.5}In_{0.5}$ compound this temperature equals about 10 K. However for SmPdIn it is even higher than for two other samarium compounds and equals 38 K. In this case the

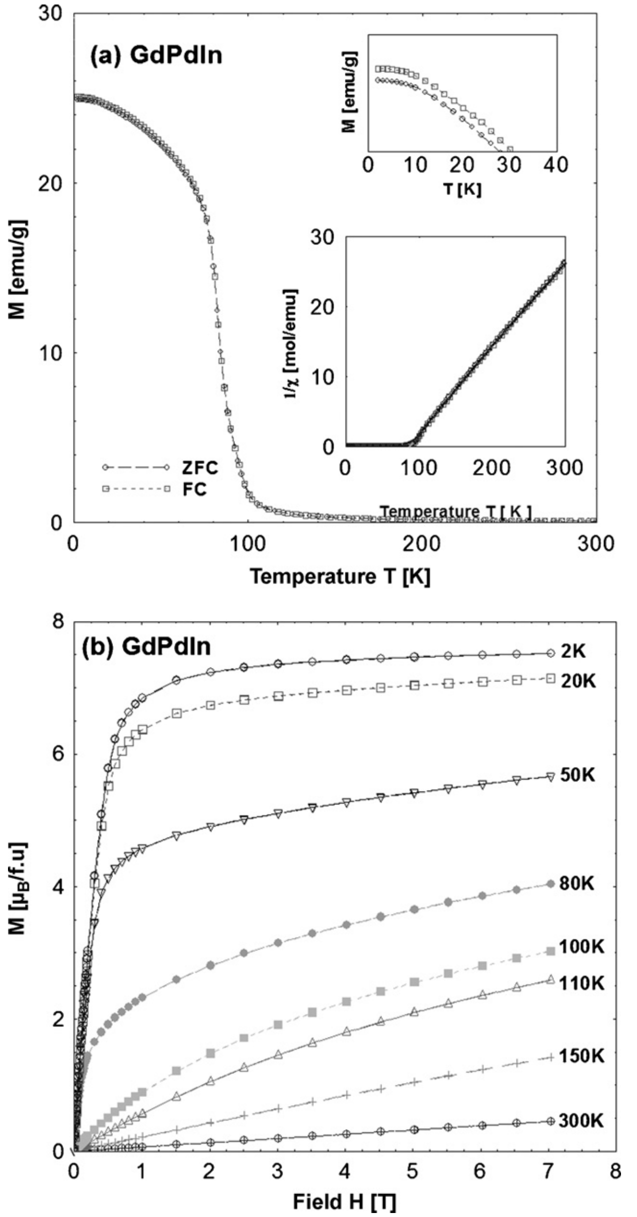

Fig. 5. (a) Temperature variation of magnetization of the GdPdIn compound in 0.1 T. The upper inset shows $M(T)$ in low temperature range. The lower inset represents $1/\chi\,(T)$ dependence. (b) The magnetic isotherms measured in the temperature range 2–300 K up to 7 T for the GdPdIn compound.

magnetic isotherms obtained suggest ferri or ferromagnetic ordering below the characteristic temperature. Similar behaviour was already observed for SmPtMg [6]. The value of this temperature is lower than observed before for the SmPdIn single crystal where $T_C = 54$ K [4].

The susceptibility for Sm-rich compounds exhibits non Curie–Weiss behaviour (NCW). It is connected with of temperature independent Van Vleck contribution. This contribution is associated with the second-order Zeeman effect which is important in samarium compounds with narrow multiplet width of trivalence Sm ions.

The substitution of Gd rare earth element with higher 4f and 5d electron numbers in the place of Sm causes the change of some magnetic properties. In the $Gd_xSm_{1-x}PdIn$ compounds the temperature dependence of magnetization $M(T)$ is typical of a ferromagnet, rises rapidly with lowering the temperature below T_C and then saturates at low temperatures. For compounds where $x = 0.5$ and $x = 1.0$ the Curie temperature is higher than in SmPdIn and the inverse susceptibility follows modified Curie–Weiss (CW) behaviour in the temperature range 100–300 K with the temperature independent susceptibility χ_0. The values of T_C equal 60 K and 83 K for $x = 0.5$ and 1.0, respectively. The other obtained parameters are: $\theta_p = 61.3$ K, $\mu_{eff} = 5.14\,\mu_B$/f.u., $\chi_0 = 2.9 \times 10^{-3}$[emu/mol] and $\theta_p = 86.3$ K, $\mu_{eff} = 7.73\,\mu_B$/f.u., $\chi_0 = 2.7 \times 10^{-3}$[emu/mol] for $x = 0.5$ and $x = 1.0$, respectively (see Table 1). Replacement Sm by Gd causes the increase of effective magnetic moment deduced from Curie constant because for free Sm^{3+} ion μ_{eff} is much more lower ($0.84\,\mu_B$) than for free Gd^{3+} ($7.94\,\mu_B$) ion. However the effective magnetic moment in all studied compounds is smaller than for free Gd^{3+} ion.

Let consider the magnetization isotherms measured in the 2–300 K temperature range and in the applied magnetic filed up to 7 T $M(H)$. One can notice that the visible difference occurs between isotherms for compounds where Sn is substituted by In and where Sm is substituted by Gd. The $M(H)$ magnetization curves for the SmPdSn and $SmPdSn_{0.5}In_{0.5}$ compounds are linear in the whole temperature range. Moreover, for SmPdSn the value of $M(H)$ at 7 T raises with temperature up to 12.35 K and next decreases that can be a confirmation of the pure antiferromagnetic order.The field variation of magnetization $M(H)$ is quite different for the SmPdIn compound. The magnetization at 7 T is almost saturated and equals $0.21\,\mu_B$/f.u. This value is the same as observed before for easy axis in the SmPdIn single crystal [4]. The Sm/Gd substitution causes the increase of $M(H)$ values which equal $3.36\,\mu_B$/f.u. and $7.52\,\mu_B$/f.u. for $x = 0.5$ and $x = 1.0$, respectively (Table 1). However the value of M_S for GdPdIn is smaller than for free Gd ion. The M_S at 7 T is larger in Gd-rich compounds which is due to the larger moment of Gd^{3+} ion ($7\,\mu_B$) as compared to that of Sm^{3+} ion ($0.71\,\mu_B$).

3.2. *The magnetocaloric effect (MCE) in the $SmPdSn_{1-x}In_x$ and $Gd_xSm_{1-x}PdIn$ compounds*

The magnetocaloric effect (MCE) is the response of a magnetic material to the application of the magnetic field [7–10]. Due to the coupling of the magnetic sublattice with the applied magnetic field in the ferromagnetic compounds near by T_C the unpaired 4f or 3d electrons are arranged with the field. It causes the decrease of the magnetic entropy in the isothermal process or warm up the sample on the adiabatic process. In a reversible demagnetizating effect when the magnetic field is removed the spins come back to the chaotic orientation and the entropy is reduced what is reflected in

Table 1
Magnetic properties of studied compounds.

Compound	$T_{N,C}$ (K)	θ_p(K)	μ_{eff} [μ_B/f.u.]	M [μ_B/f.u.] at 2 K and 7 T	$-\Delta S_M$[J/kg K] $\Delta\mu_0 H = 1$ T	$-\Delta S_M$[J/kg K] $\Delta\mu_0 H = 7$ T
SmPdSn	4.5 12.5	–	–	0.01	0.0012	0.0436
$SmPdSn_{0.5}In_{0.5}$	10	–	–	0.45	0.0013	0.0610
SmPdIn	38	–	–	0.21	0.0764	0.5515
$Sm_{0.5}Gd_{0.5}PdIn$	60	61.3	5.14	3.36	0.9181	5.6240
GdPdIn	83	86.3	7.73	7.52	0.9503	6.2124

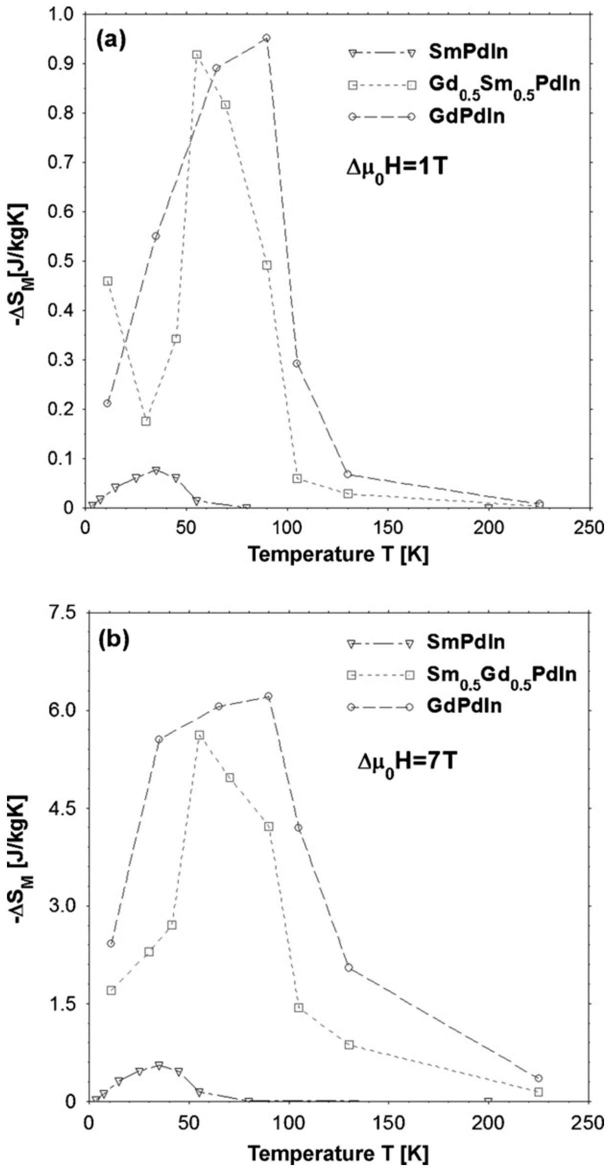

Fig. 6. Variation of isothermal magnetic entropy of the $SmPdSn_{1-x}In_x$ and the $Gd_xSm_{1-x}PdIn$ compounds at (a) $\Delta\mu_0H = 1$ T, (b) $\Delta\mu_0H = 7$ T.

the cooling of the material.

$$\Delta S_m(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'$$

The MCE can be evaluated from the calculated magnetic entropy change $\Delta S_m(T,H)$ according to formula:

The $\Delta S_m(T,H)$ is calculating from the isothermal magnetization curves of the studied compounds as a function of temperature in the magnetic field of 0–7 T.

The $\Delta S_m(T,H)$ change in the $SmPdSn_{1-x}In_x$ and $Gd_xSm_{1-x}PdIn$ compounds as a function of temperature at $\Delta\mu_0H = 1$ T exhibit maximum around the temperature of magnetic phase transition and is the highest for Gd rich samples (0.9503 J/kg K for GdPdIn) and decreases with the increasing of Sm (Fig. 6a) The increase of applied magnetic field causes the increase of $\Delta S_m(T,H)$ for all investigated samples. The highest value of $\Delta S_m(T,H)$ was observed at 7 T for GdPdIn compound and equals 6.2124 J/kg K (Fig. 6b). The MCE in these two series most of all depends on the 4f spin.

4. Concluding remarks

From all measurements performed for the $SmPdSn_{1-x}In_x$ ($x = 0.0$, 0.5, 1.0) and $Gd_xSm_{1-x}PdIn$ ($x = 0.0$, 0.5, 1.0) compounds the following conclusions can be drawn:

- The thermomagnetic irreversibility at 0.1 T for all studied compounds is very small. The highest difference between ZFC and FC curves was noticed for the SmPdSn and GdPdIn compounds. The temperature of magnetic phase transition as well as the value of magnetic moment at 7 T is the highest for Gd – rich compounds. The susceptibility for Sm-rich compounds exhibits non Curie–Weiss behaviour (NCW) whereas for compounds containing Gd follows modified Curie–Weiss (CW) law.
- The $M(H)$ magnetization curves for SmPdSn and $SmPdSn_{0.5}In_{0.5}$ are not saturated. It may be connected with the antiferromagnetic order. For $Gd_xSm_{1-x}PdIn$ studied compounds $M(H)$ is almost saturated at 7 T. The value of M_S equals 0.21 μ_B/f.u., 3.36 μ_B/f.u. and 7.52 μ_B/f.u. for $x = 0.0$, $x = 0.5$ and $x = 1.0$, respectively.
- The change of magnetic entropy $\Delta S_m(T,H)$ in $SmPdSn_{1-x}In_x$ and $Gd_xSm_{1-x}PdIn$ is the highest for Gd rich samples (0.9503 J/kg K for GdPdIn at 1 T) and decreases with the increasing of Sm content. The MCE in these two series most of all depends on the 4f spin. The increase of applied magnetic field up to 7 T causes the increase of $\Delta S_m(T,H)$ for all investigated samples.

References

[1] D.T. Adroja, S.K. Malik, Phys. Rev. B 45 (1992) 779.
[2] M. Bałanda, A. Szytuła, M. Guillot, J. Magn. Magn. Mater. 247 (2002) 345.
[3] J. Skurai, K. Kegai, T. Kuwai, Y. Isikawa, K. Nishimura, K. Mori, J. Magn. Magn. Mater. 140–144 (1995) 875.
[4] T. Ito, K. Ohkubo, T. Hirasawa, J. Takeuchi, I. Hiromitsu, M. Kurisu, J. Magn. Magn. Mater. 140–144 (1995) 873.
[5] Ł. Gondek, A. Szytuła, D. Kaczorowski, K. Nenkov, Solid State Commun. 142 (2007) 556.
[6] R. Kraft, G. Kotzyba, R.-D. Hoffmann, R. Pöttgen, Z. Naturforsch. 57b (2002) 488.
[7] V.K. Pecharsky, K.A. Gschneider, JMMM 200 (1999) 44.
[8] V.K. Pecharsky, K.A. Gschneider, Int. J. Refrig. 29 (2006) 1239.
[9] B.F. Yu, Q. Gao, B. Zhang, X.Z. Meng, Z. Chen, Int. J. Refrig. 26 (2003) 622.
[10] V.K. Pecharsky, K.A. Gschneider, J. Rare Earths 24 (2006) 641.