Magnetocaloric effect of GdTX (T = Mn, Fe, Ni, Pd, X=Al, In) and GdFe$_6$Al$_6$ ternary compounds

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Abstract. The investigations of the magnetocaloric properties of GdTX (T=Mn, Fe, Ni, Pd, X=Al, In) and GdFe$_6$Al$_6$ ternary compounds for possible applications in magnetic refrigeration are presented. Magnetization measurements have been performed in the temperature range of 2-300 or 400 K and magnetic field range of 0-7 T. The magnetic entropy changes $\Delta S_m$ have been calculated indirectly from the magnetization measurements. The calculated values of entropy change $\Delta S_m$ for examined compounds amount -13.63 J/Kkg, -13.05 J/Kkg, -6.13 J/Kkg, -3.72 J/Kkg, -1.38 J/Kkg and -0.94 J/Kkg respectively for GdNiAl, GdPdAl, GdPdIn, GdFeAl, GdFe$_6$Al$_6$ and GdMnAl at 7 T.

1. Introduction
It is known that applying external magnetic field to a magnetic material under adiabatic conditions change the spins alignment. When the magnetic field is applied the magnetic spins attempt to align parallel to the magnetic field. It causes increase of the magnetic order and consequently the temperature will rise due to magnetocaloric effect. When the magnetic field is removed the spins become again randomly oriented and the material cools down.

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$_x$)$_4$ [1, 2], MnFe$_x$(P$_{1-x}$As$_x$)$_2$, Mn(As$_{1-x}$Sb$_x$)$_2$ and also La(Fe$_{1-x}$Si$_x$)$_3$ [3, 4] reveal a considerable magnetocaloric effect (MCE).

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) [5]. 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 [6]. 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 calculate a magnetocaloric effect of polycrystalline samples of intermetallic compounds GdTX (T = metal 3d, 4d, 5d; X = metal sp) and GdFe$_6$Al$_6$. The calculations of the magnetic entropy change, $\Delta S_m$, 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. GdFeAl, GdNiAl and GdPdAl were then annealed at 850°C for 1 week. Crystalline phase identification was carried out by power X-ray diffraction with Cu (Kα) radiation using a Siemens D-5000 diffractometer. The determined lattice constants were in good agreement with the data reported in Refs. [7, 8, 9, 10, 11, 12].

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

The isothermal magnetization curves \(M(\mu_0 H)\) of GdMnAl, GdFeAl, GdPdAl, GdNiAl, GdPdIn and GdFe₆Al₆ intermetallics compounds were measured in magnetic field up to 7 T. The calculations of the magnetic entropy change, \(\Delta S_m\), were performed using the isothermal magnetization curves. To determine \(\Delta S_m\) from magnetization measurements following equation was used:

\[
\Delta S_m = \sum_{i=1}^{n} \frac{M(T_{i+1}, H) - M(T_i, H)}{T_{i+1} - T_i} \Delta H
\]

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 \(\Delta S_m\) is the magnetic entropy change.

Some example data of the isotherm magnetization curves for GdNiAl are shown in Fig. 1. Figure 2 presents the temperature dependence of the entropy change for different magnetic field variations for GdNiAl. The maximum value of the entropy change is located near the magnetic transition temperature of the GdNiAl, (\(T_C = 57\) K). The maximum entropy change value obtained at 3, 5 and 7 T amounts -7.19 J/Kkg, -10.6 J/Kkg and -13.63 J/Kkg, respectively. The calculated values of the \(\Delta S_m\) were in good agreement with the data reported in Refs. [13, 14].

![Figure 1. Isotherm magnetization curves of GdNiAl.](image1)

![Figure 2. Calculated entropy change for different magnetic field variations for GdNiAl.](image2)
The observed anomalies below 100 K is also visible in the $\Delta S_m(T)$ curve as the second peak.

**Figure 3a-e.** Calculated entropy change for different magnetic field variations for a) GdPdAl, b) GdPdIn, c) GdFeAl, d) GdFe$_6$Al$_6$, e) GdMnAl.

**Figure 4.** The ac susceptibility of GdMnAl.
The comparison of the magnetocaloric properties of GdTX (T=Mn, Fe, Ni, Pd, X=Al, In) and GdFe₆Al₆ is shown in Table 1. Figure 5 shows the calculated entropy change for above compounds at magnetic field of 2 T.

**Table 1.** The comparison of magnetic entropy change |ΔSₘ| for GdTX (T=Mn, Fe, Ni, Pd, X=Al, In) and GdFe₆Al₆.

| Compound   | Transition temperature | |ΔSₘ| [J/K kg] |
|------------|------------------------|| 2 T | 5 T | 7 T |
| GdNiAl     | 57 K                   | 5.17 | 10.6 | 13.63 |
| GdPdAl     | 46 K                   | 5.57 | 10.41 | 13.05 |
| GdPdIn     | 90 K                   | 2.08 | 4.64 | 6.13 |
| GdFeAl     | 200 K                  | 1.22 | 2.78 | 3.72 |
| GdFe₆Al₆   | 334 K                  | 0.56 | 1.1 | 1.38 |
| GdMnAl     | 274 K                  | 0.31 | 0.69 | 0.94 |

In conclusion, the investigations of the magnetocaloric effect in GdTX (T=Mn, Fe, Ni, Pd, X=Al, In) and GdFe₆Al₆ were presented. The highest value of MCE for GdNiAl and GdPdAl was found. 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 [8, 16]. Therefore, the large magnetocaloric effect may be connected with isostructural transitions. For all investigated compounds the maximum value of the entropy change is located near the magnetic temperature transition of the magnetic material. It is also clear visible that the MCE increases with the increase of applied magnetic field. Polycrystalline samples give some benefit to application due to lack of anisotropy and magnetic hysteresis in the most important region. The GdNiAl, GdPdAl and GdPdIn display interesting magnetocaloric properties. However, due to cost of materials and not very high ordering temperatures above compounds are not very promising candidates for practical room-temperature magnetic refrigeration. The GdFeAl, GdFe₆Al₆ and GdMnAl exhibit ordering temperature near room temperature and the half-height width of the MCE peaks are large enough in order to be used as an active magnetic refrigerator in a wide range of the temperature. Unfortunately low values of the entropy change make their application almost impossible.
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