Journal of Alloys and Compounds 680 (2016) 415–418

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Magnetic properties and magnetocaloric effect in Tm-based magnesium compounds Tm_4PdMg and Tm_4PtMg

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ARTICLE INFO

Article history:
Received 18 March 2016
Received in revised form
13 April 2016
Accepted 16 April 2016
Available online 20 April 2016

Keywords:
Magnetocaloric effect
Tm_4PdMg
Tm_4PtMg
Magnetic properties
Magnetic phase transition

ABSTRACT

The magnetic and the magnetocaloric properties of Tm_4PdMg and Tm_4PtMg have been investigated. A second order magnetic phase transition from a paramagnetic to a ferromagnetic state was observed for Tm_4PdMg and Tm_4PtMg at the Curie temperatures of T_C ~6.0 and 4.5 K, respectively. A large reversible magnetocaloric effect was observed for both compounds at low temperature. For a magnetic field change of 7 T, the values of maximum magnetic entropy change ($-\Delta S_M^{max}$), refrigerant capacity (*RC*) and relative cooling power (*RCP*) are 18.0 J/kg K, 319 J/kg and 414 J/kg for Tm_4PdMg, and 16.5 J/kg K, 275 J/kg and 353 J/kg for Tm_4PtMg, respectively.

1. Introduction

The magnetocaloric effect (MCE) is an intrinsic thermal response of all magnetic materials when the material is exposed to a varying magnetic field. Magnetic refrigeration based on MCE is considered to be a promising alternative technology over the conventional gas compression/expansion refrigeration due to its higher energy efficiency and more environmental conservation [1–3]. To search for active magnetic refrigeration materials, many rare-earth based intermetallic compounds have been synthesized and systematically investigated with respect to the magnetic properties and MCE, and some of them are found to possess excellent magnetocaloric properties [4–10].

Many magnetocaloric materials are based on rare earths (*RE*) and especially rare earth-rich phases are promising candidates. A broad family of such materials are the cubic RE_4TX (T = Ru, Rh, Pd, Ir, or Pt; X = Al, In, Mg, Cd) intermetallics with Gd_4RhIn-type structure [11]. So far, more than 200 representatives of this type have been reported [12]. Some property studies (magnetism, transport properties, hydrogenation behaviour, etc.) were reported for the magnesium compounds RE_4TMg [13–15]. Recently, we have systematically investigated the magnetic properties and MCE in RE_4PtMg (*RE* = Ho and Er) and RE_4PdMg (*RE* = Eu and Er) compounds [16–18], respectively. A second order magnetic phase transition was revealed at Curie temperatures of T_C ~28, 21, 16, and 150 K for Ho_4PtMg, Er_4PtMg, Er_4PdMg, and Eu_4PdMg, respectively. A large reversible MCE was observed around T_C for all studied compounds. For a field change of 0–7 T, the maximum values of the magnetic entropy change ($-\Delta S_M^{max}$) are 16.9, 20.6, 22.5, and 7.2 J/kg K for Ho_4PtMg, Er_4PtMg, Er_4PdMg, and Eu_4PdMg, respectively. The corresponding values of relative cooling power (*RCP*) were evaluated to be 762, 742, 716, and 1346 J/kg [16–18].

Very recently, the magnetism and MCE in several Tm-based intermetallic compounds have been reported [19–22], and a giant low-field MCE was found in TmCuAl and TmZn, respectively, which is beneficial for active application [21,22]. In continuation of these studies, we synthesized Tm_4PdMg and Tm_4PtMg and investigated their magnetic and magnetocaloric properties. Characteristics of the magnetic phase transition and the origin of large MCE are discussed.

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http://dx.doi.org/10.1016/j.jallcom.2016.04.154

2. Experimental

High quality polycrystalline samples of Tm_4PdMg and Tm_4PtMg were synthesized from high purity Tm, Pd, Pt, and Mg (all better than 99.9%). Stoichiometric amounts of the elements were weighed and arc-welded [23] in tantalum tubes under an argon pressure of ~80 kPa. Then the tantalum tubes were placed in a water-cooled sample chamber of an induction furnace [24] and heated up to 1220 K for 4 min, following by 180 min annealing at 920 K. Both samples were proved to be single phase by X-ray powder diffraction (Rigaku RINT 2200 diffractometer, Cu radiation) and Energy Dispersive X-ray Spectroscopy (Zeiss EVO MA10 scanning electron microscope equipped with EDX) at room temperature. The refined lattice parameters of our samples (a = 1357(6) pm for Tm_4PdMg and a = 1358(4) pm for Tm_4PtMg) are in good agreement with the literature data [15]. The magnetization measurements were performed with a commercial vibrating sample magnetometer (VSM) which is an option of the physical properties measurement system (PPMS-9, Quantum Design).

3. Results and discussion

The temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization (M) for Tm_4PdMg and Tm_4PtMg under the magnetic fields (H) of 0.05–0.2 T are shown in Fig. 1 (a) and (b), respectively. The ZFC and FC $M(T)$ curves for both compounds show a typical paramagnetic to ferromagnetic (PM-FM) transition at Curie temperatures of T_C ~ 6.0 and 4.5 K, respectively. Only very tiny differences can be observed between ZFC and FC M-T curves under low magnetic fields for both compounds, which is usually the case for magnetic materials possessing a second order magnetic transition. The magnetization susceptibility ($\chi = M/H$, left scale) and the reciprocal susceptibility ($1/\chi$, right scale) under $H = 1$ T for Tm_4PdMg and Tm_4PtMg as a function of temperature are shown in Fig. 2 (a) and (b), respectively. The high temperature reciprocal susceptibility shows Curie-Weiss behaviour. The evaluated value of the effective magnetic moment is 7.63 and 7.68 μ_B/Tm for Tm_4PdMg and Tm_4PtMg, respectively, which is close to the free ion value of Tm^{3+} (7.56 μ_B).

To evaluate the MCE in Tm_4PdMg and Tm_4PtMg, a set of magnetic isotherms $M(H)$ with increasing and decreasing magnetic field up to 7 T for both compounds were measured. All the $M(H)$ curves show completely reversible behaviour during the cycles with increasing and decreasing field, which is beneficial for practical applications. To ensure the readability of the figure, only several isotherms with increasing field are presented in Fig. 3 (a) and (b) for Tm_4PdMg and Tm_4PtMg, respectively. According to the Banerjee criterion [25], the magnetic transition is of first order if some of the μ_0H/M versus M^2 curves (also named as Arrott plot) show negative slope. On the other hand, if all the Arrott plots are positive, the magnetic transition is of second order. Thus, the measured M-H curves for Tm_4PdMg and Tm_4PtMg were converted in to μ_0H/M versus M^2 plot (Fig. 4 (a) and (b)). Only positive slopes can be observed in the Arrot plots for Tm_4PdMg and Tm_4PtMg, indicating the occurrence of a second order magnetic transition for both compounds.

The magnetic entropy change $-\Delta S_M$ was calculated from the $M(H)$ curves at different temperatures by integrating the Maxwell's relation,

$$\Delta S_M(T, \Delta H) = \int_0^{H^{\max}} (\partial M(H,T)/\partial T)_H dH. \quad (1)$$

The resulting temperature dependence of $-\Delta S_M$ with various magnetic field changes up to 0–7 T for Tm_4PdMg and Tm_4PtMg are shown in Fig. 5 (a) and (b), respectively. With the magnetic field changes of 0–2, 0–5, and 0–7 T, the maximum values of magnetic entropy change ($-\Delta S_M^{max}$) are evaluated to be 7.0, 14.9, and 18.0 J/kg for Tm_4PdMg and 6.0, 13.7, and 16.5 J/kg K for Tm_4PtMg, respectively. The observed values of the$-\Delta S_M^{max}$ under the magnetic field change of 0–5 T for the present Tm_4PdMg and Tm_4PtMg are

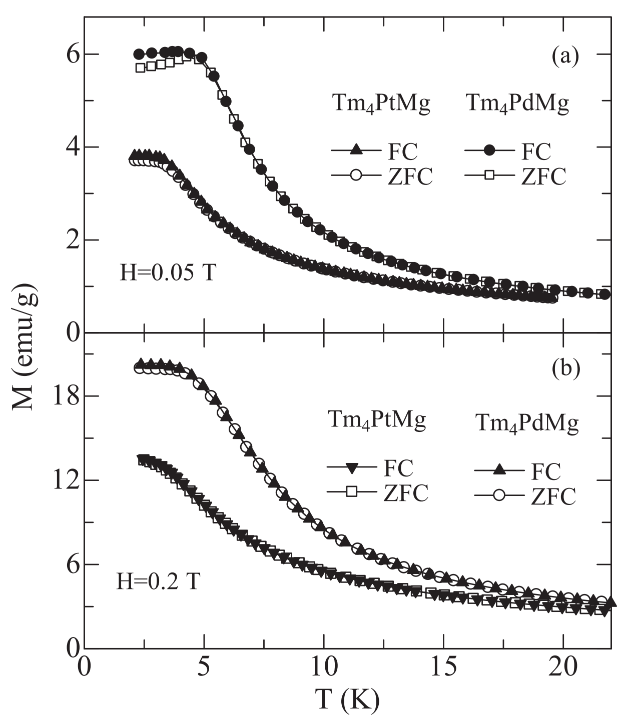

Fig. 1. Temperature dependence of the zero field cooled (ZFC) and field cooled (FC) magnetization (M) under the magnetic fields (H) of 0.05 (a) and 0.2 T (b) for Tm_4PdMg and Tm_4PtMg.

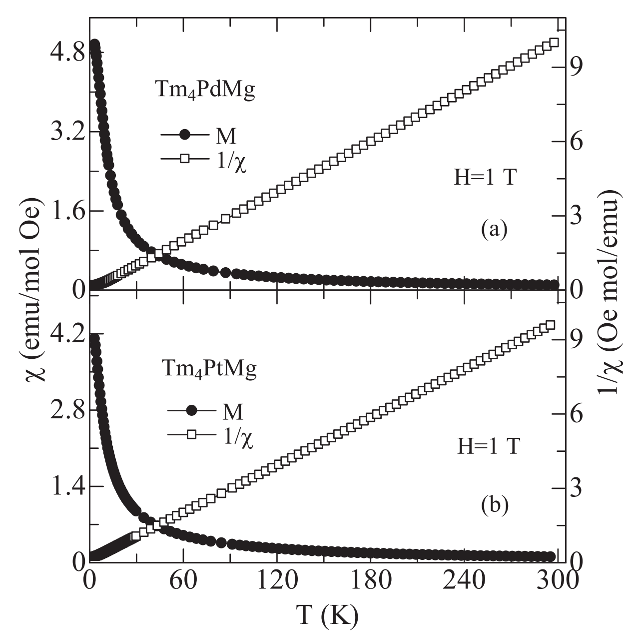

Fig. 2. Temperature dependence of magnetization (M, left scale) and the reciprocal susceptibility ($1/\chi = H/M$, right scale) under the magnetic field of $H = 1$ T for Tm_4PdMg (a) and Tm_4PtMg (b).