

Magnetic and Magnetocaloric Properties of $(\text{Gd}_{1-x}\text{Ce}_x)\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) Compounds

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(Received 8 July 2011, Received in final form 3 October 2011, Accepted 4 October 2011)

The magnetic and magnetocaloric properties of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic compounds alloys have been investigated in detail for the first time. XRD patterns indicated that all the samples were crystallized in a single phase with MgCu_2 -type structure (Laves phase). Ce substitution for Gd increased the lattice parameters and decreased the Curie temperature from 163 K for $x = 0$ to 37 K for $x = 0.75$. A maximum entropy change of 3.82 J/kg K was observed when a 2 T magnetic field was applied to the $x = 0$ sample. This entropy change decreased with increasing Ce content to 2.04 J/kg K for the $x = 0.75$ sample.

Keywords : magnetic properties, magnetocaloric effect, intermetallic compounds, laves phase

1. Introduction

Magnetic refrigerators based on the magnetocaloric (MC) effect, which is the temperature change of a magnetic material associated with an external magnetic field change, have attracted considerable attention. The interest in magnetocaloric materials is due to the possibility of their practical application in magnetic refrigerators which are an alternative to conventional vapour compression refrigerators [1-4]. Nowadays, nearly all the studies on the magnetocaloric effect (MCE) and magnetic cooling have focused on the search for the most suitable magnetic materials, which are those with the largest magnetocaloric effects. Up to now, many magnetic amorphous and crystalline materials have been suggested as potential candidates for use in magnetic refrigeration technology near room temperature [5-10].

Recent studies have verified that intermetallic RAl_2 (R = rare earth) compounds with cubic Laves-phase could be promising candidates for magnetic refrigeration technology due to their relatively large magnetic entropy change [11-27]. Therefore, the magnetic and magnetocaloric properties of several intermetallic compounds, such as DyAl_2 [11, 12], TbAl_2 [13], ErAl_2 [14], PrAl_2 [15-17] and GdAl_2 [18-20], and their alloys, such as $\text{Gd}_{1-x}\text{Pr}_x\text{Al}_2$ [15],

$\text{Gd}_{1-x}\text{Er}_x\text{Al}_2$ [14, 21], $\text{Tb}_{1-x}\text{Y}_x\text{Al}_2$ [22], $\text{Er}_{1-x}\text{Tb}_x\text{Al}_2$ [23], $\text{Dy}(\text{Al}_{1-x}\text{Co}_x)_2$ [24], $\text{Gd}(\text{Al}_{1-x}\text{Fe}_x)_2$ [18, 25, 26] and $\text{Gd}(\text{Al}_{1-x}\text{Co}_x)_2$ [27], have recently been intensively investigated. These recent studies have showed that the ground state for most intermetallic Laves compounds is ferromagnetic. Among these materials, GdAl_2 is ferromagnetic with a Curie temperature between 153 and 182 K [28, 29]. Jianqiu *et al.* [27] have reported that the maximum magnetic entropy change of GdAl_2 is 4 J/kg K for a magnetic field of 2 T and the Curie temperature is 165 K. Despite the fact that its Curie temperature is relatively low compared to room temperature, GdAl_2 shows a relatively large MCE. In many previous studies on intermetallic Laves compounds (RAl_2), it has been shown that the Curie temperature can be adjusted by alloying with appropriate transition metal or rare-earth elements [14-27]. The relatively large MCE and adjustable Curie temperatures of intermetallic RAl_2 compounds make them attractive candidates for magnetic refrigeration.

It has been reported that Ce substitution has a great influence on the Curie temperature, magnetization curve, and magnetocaloric properties of Gd-based materials [30, 31]. Therefore, in this study, the influence of substitution of Gd with Ce on the structural, magnetic and magnetocaloric properties of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic Laves compounds has been investigated in detail for the first time.

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2. Experimental

$\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0; 0.25; 0.5; 0.75$) compounds were prepared by arc melting in a highly pure (99.9%) argon gas atmosphere. The highly pure (99.9 + %) ingots were turned over and melted four times to ensure their homogeneity. The resulting buttons were sealed in a quartz tube under high vacuum and annealed at 1273 K for 5 hours to homogenize the material. In all the heat treatments, the sealed samples were directly placed into a pre-heated furnace at 1273 K and after the annealing process the samples were slowly cooled to room temperature. The structures of the $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0; 0.25; 0.5; 0.75$) samples were investigated by an X-ray diffractometer (Rigaku-Radb) system. X-ray diffractograms were recorded with a power diffractometer at room temperature using $\text{CuK}\alpha$ radiation. The magnetic measurements of the $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0; 0.25; 0.5; 0.75$) samples were performed using a Q-3398 (Cryogenic) magnetometer in a temperature range from 50 to 250 K with the application of a 6 T maximum magnetic field.

3. Results and Discussion

Fig. 1 shows the XRD patterns of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic compounds at room temperature. The XRD patterns indicate that all the samples have a single C15 cubic Laves phase (MgCu_2 type structure) and no impurity phase has been detected. The lattice parameters of the single phase alloys are listed in Table 1. The lattice parameter of undoped GdAl_2 ($x = 0$) is about 7.915 Å, which agrees with the literature value of 7.913 Å [15, 27]. Ce substitution leads to an almost linear increase in the lattice parameter from 7.913 Å for $x = 0$ to 8.026 Å for $x = 0.75$. In Ce-doped samples the linear increase in the lattice parameter may occur because the Ce atomic radius is larger than that of Gd. Similar variations in lattice parameters were reported for $\text{Gd}_{1-x}\text{Pr}_x\text{Al}_2$ [15] and $\text{Er}_{1-x}\text{Dy}_x\text{Co}_2$ [32] alloys, where the atomic radii of Pr and Dy are larger than those of the substituted atoms, as in the case of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$.

Fig. 2 shows the temperature dependence of the mag-

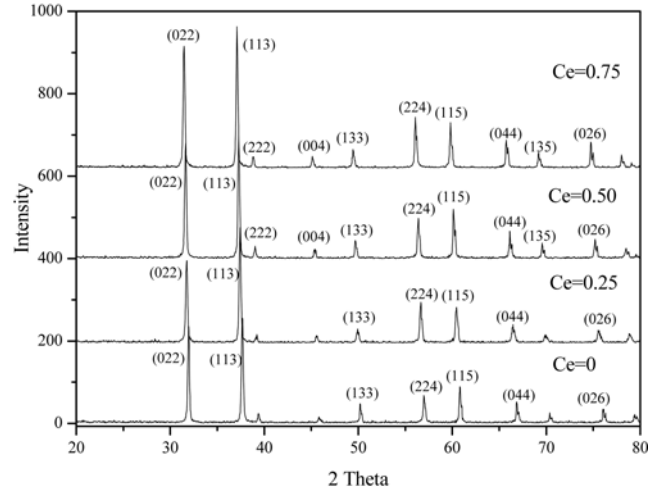


Fig. 1. XRD patterns of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic compounds at room temperature.

netization for $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic samples. Data were taken for an applied magnetic field of 0.1 T. It can be seen that a transition from ferromagnetic to paramagnetic phase occurs in all the samples near the Curie temperature. The Curie temperature can be defined as the temperature at which the value

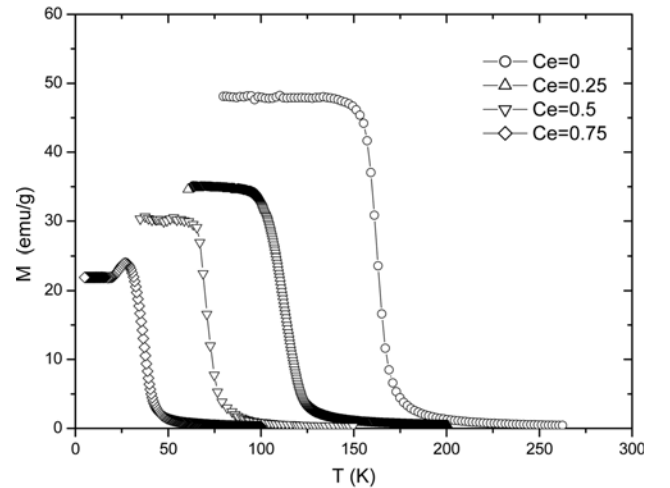


Fig. 2. Temperature dependence of the magnetization of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) alloys at 0.1 T magnetic field.

Table 1. Lattice parameter (a), Curie temperature (T_c), B constant, spin-wave stiffness constant (D), exchange constant (J_{exc}), and maximum entropy change ($|\Delta S_m|$) in $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ alloys

x	a (Å)	T_c (K)	B ($\text{K}^{-3/2}$)	D ($\text{meV}/\text{Å}^2$)	J ($\text{meV}/\text{Å}$)	ΔS_m (J/kgK)
0	7.915	163	2.92×10^{-6}	944.98	8.279	3.82
0.25	7.955	113	4.04×10^{-6}	948.17	5.974	3.23
0.5	7.986	70	3.00×10^{-5}	271.86	1.502	3.47
0.75	8.026	37	3.38×10^{-2}	3.115	0.012	2.04

of $|dM/dT|$ is maximized. It was measured to be 163 K for $x = 0$, 113 K for $x = 0.25$, 70 K for $x = 0.5$, and 37 K for $x = 0.75$. The Curie temperatures are listed in Table 1. The measured value of the Curie temperature for GdAl_2 ($x = 0$) is approximately in agreement with literature values reported in Refs. [27-29]. It is clearly seen that Ce substitution slightly decreases the Curie temperatures of the samples. In the rare-earth transition-metal (RE-TM) compounds, the Curie temperatures are determined by three kinds of interactions: TM-TM, RE-TM and RE-RE. Among these, the TM-TM interaction is usually the strongest and is therefore dominant [26]. In the GdAl_2 compound, because the transition-metal sublattice consists of non-magnetic Al atoms, the TM-TM and RE-TM interactions are neglected. Only one magnetic sublattice exists. Due to the one-sublattice model, only the ferromagnetic Gd-Gd interaction exists in GdAl_2 which explains why GdAl_2 is ferromagnetic [26, 27]. To understand the exchange interactions in $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ alloys, a two-sublattice model (where the two sublattices are the Gd-sublattice and the Ce-sublattice) must be used. Due to the two-sublattice model [18, 27, 33, 34], there are three types of exchange interactions in $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ alloys, Gd-Gd, Gd-Ce and Ce-Ce interactions, which have to be taken into account. In $\text{RE}_{1-x}\text{RE}'_x\text{Al}_2$ (where RE and RE' = rare earth elements) type alloys, the nature of the magnetic ordering and the Curie temperature are strongly dependent on the inter-sublattice exchange interactions, and therefore on the spin-orbit couplings [32] between rare-earth elements. In many previous studies it has been reported that in systems in which either both rare-earth elements are light (from Ce to Sm) or both are heavy (from Gd to Yb), the resulting exchange coupling is ferromagnetic, whereas for light-heavy combinations the exchange coupling is ferrimagnetic [15, 29, 35]. Recent experimental and theoretical works have confirmed the existence of ferrimagnetic coupling in $\text{Gd}_{1-x}\text{Pr}_x\text{Al}_2$ alloys [15, 29]. In $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ compounds, due to the light-heavy combination of Ce and Gd atoms, the resulting exchange interaction between Gd-Ce is expected to be ferrimagnetic. This ferrimagnetic behavior is clearly seen in the magnetization curve for the $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{Al}_2$ sample in Fig. 2. Due to the anti-parallel arrangement of Gd and Ce spins, the ferromagnetic interaction weakens and consequently the Curie temperature decreases. In order to elucidate the influence of Ce doping on the thermal variation of the magnetization and the Curie temperature, the spin-wave dispersion coefficient D and exchange constant J_{exc} were calculated using Bloch's $T^{3/2}$ law, as given in the following equation [36],

$$M(T) = M(0)[1 - BT^{3/2}] \quad (1)$$

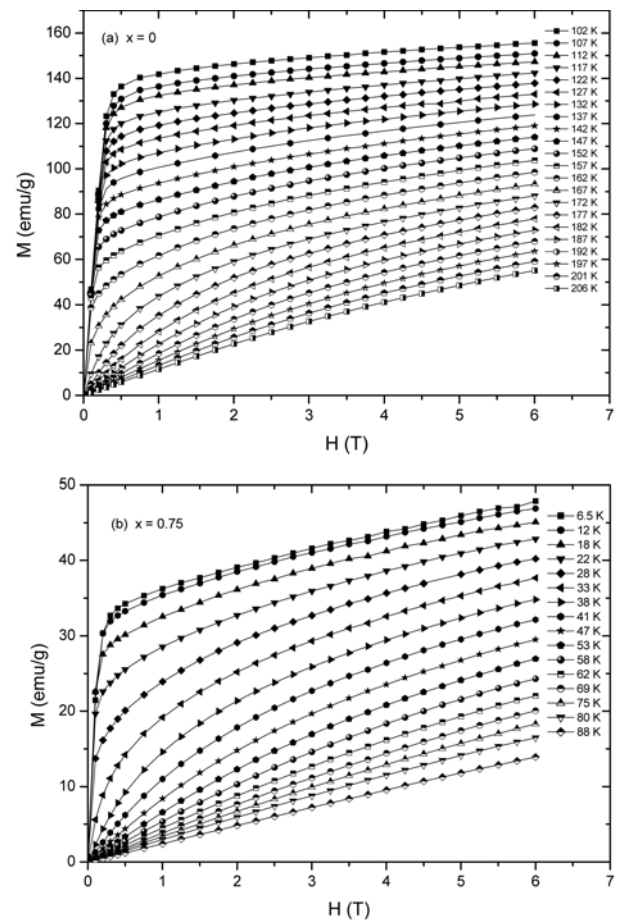


Fig. 3. Magnetic field dependence of the magnetization measured at different temperatures for $x = 0$ and $x = 0.75$ samples.

where $M(0)$ is the magnetization at zero temperature and B is the Bloch constant, obtained by fitting Eq. (1) to the experimental magnetization curves (Fig. 2) in the low temperature range. The Lande g factor was taken from [29] directly. The estimated parameters are listed in Table 1. The value of the exchange constant, J_{exc} , decreases from 8.279 meV/Å for $x = 0$ to 0.0124 meV/Å for $x = 0.75$. The decrease in J_{exc} with increasing Ce content is a clear evidence of the weakening of the ferromagnetic interaction.

Fig. 3 shows the variation of the magnetization as a function of applied magnetic field at different temperatures for the $x = 0$ and $x = 0.75$ samples. The magnetization isotherms for the $x = 0$ sample (Fig. 3a) show typical ferromagnetic behavior. Below the Curie temperature, the magnetization curves increased sharply at a rather low magnetic field and rapidly saturated. The maximum magnetization value determined from the magnetization curves is 155.67 emu/g for the $x = 0$ sample in a 6 T magnetic field. However, the isothermal magnetization curves for the $x = 0.75$ sample (Fig. 3b) increase gradually and full

saturation is not observed even at 6 T. The maximum magnetization value of 47.9 emu/g at 6 T for the $x = 0.75$ sample is considerably lower than that of the $x = 0$ sample. This decrease in magnetization with increasing Ce content could be interpreted as being due to the anti-parallel arrangement of Gd and Ce spins.

The magnetic entropy, which is associated with the MC effect, can be calculated from the isothermal magnetization curves (Fig. 3) as a function of magnetic field. According to classical thermodynamic theory, the magnetic entropy change ΔS_m produced by the variation of a magnetic field from 0 to H_{\max} is given by:

$$\Delta S_m(T, H) = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH \quad (2)$$

To evaluate the magnetic entropy change S_m , a numerical approximation of the integral in Eq. (2) and the experimental M-H curves (Fig. 3) at various temperatures were used. The results for the magnetic entropy change associated with a magnetic field change of 2 T are presented in Table 1 and Fig. 4. With increasing Ce content, the temperature corresponding to the peak value of $|\Delta S_m|$ shifts to a lower value, as in the case of the Curie temperature. The maximum value of magnetic entropy change was found to be 3.82 J/kg K for GdAl_2 which is in good agreement with literature values [20, 32]. The maximum value of magnetic entropy change, $|\Delta S_m|$, first decreases with increasing Ce content, from 3.82 J/kg K for $x = 0$ to 3.23 J/kg K for the $x = 0.25$ sample, then increases to 3.47 J/kg K for $x = 0.5$ and finally decreases to 2.04 J/kg K for the $x = 0.75$ sample. The decrease of the maximum value of magnetic entropy change with increasing Ce content may be attributed to the decrease of maximum

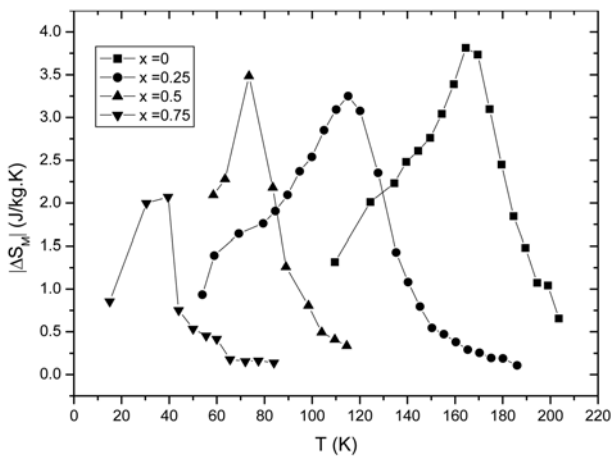


Fig. 4. Temperature dependence of the magnetic entropy change $|\Delta S_m|$ of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) samples at 2 T magnetic field.

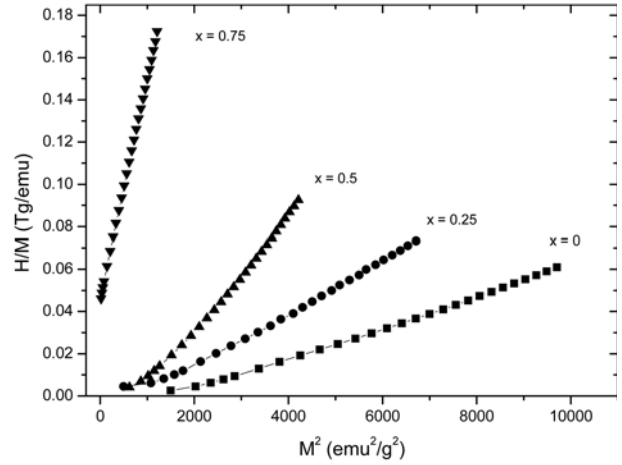


Fig. 5. Arrott plots for the $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) compounds at their Curie temperatures.

magnetization from 155.67 emu/g for $x = 0$ to 47.9 emu/g for $x = 0.75$, as this is one of the main parameters determining the value of the magnetic entropy change. Similar variations in Curie temperature and magnetic entropy change were also reported in $\text{Gd}_{1-x}\text{Pr}_x\text{Al}_2$ compounds [20].

In order to get a deeper insight in the nature of the magnetic phase transition, we plotted curves of M^2 versus H/M , which is known as an Arrott plot. Fig. 5 shows Arrott plots for the $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) compounds at their Curie temperatures. The slopes of the resulting curves denote whether a magnetic transition is of first or second order. It can be deduced that if all the curves have a positive slope, the magnetic transition is second order. On the other hand, if some of the curves show a negative slope at some point, then the magnetic transition is first order. As can be seen from Fig. 5, all the plots display nearly linear behavior at the Curie temperature and a positive slope is clearly seen over the complete M^2 range. All the properties of the Arrott plot show characteristics of a second-order magnetic phase transition.

4. Conclusions

The magnetic and magnetocaloric properties of $\text{Gd}_{1-x}\text{Ce}_x\text{Al}_2$ ($x = 0, 0.25, 0.5, 0.75$) intermetallic compound alloys have been investigated in detail for the first time. The XRD patterns indicated that all the samples crystallized in a single phase with MgCu_2 -type structure (Laves phase). Ce substitution leads to an almost linear increase in the lattice parameter from 7.913 Å for $x = 0$ to 8.026 Å for $x = 0.75$. In Ce-doped samples the linear increase in lattice parameter could be due to the fact that the Ce atomic radius is larger than that of the Gd atoms. The Curie temperature was measured to be 163 K for $x = 0$,

113 K for $x = 0.25$, 70 K for $x = 0.5$ and 37 K for $x = 0.75$. It is clearly seen that Ce substitution slightly decreases the Curie temperature. The decrease in Curie temperature was interpreted as being due to the anti-parallel arrangement of Gd and Ce spins, which causes the ferromagnetic interaction to weaken and consequently the Curie temperature decreases. The decrease in exchange interaction from 8.279 meV/\AA for $x = 0$ to 0.0124 meV/\AA for $x = 0.75$ with increasing Ce content is clear evidence of weakening of the ferromagnetic interaction. A maximum entropy change of 3.82 J/kg K was observed for the application of a 2 T magnetic field for the $x = 0$ sample. This value decreased with increasing Ce content to 2.04 J/kg K for the $x = 0.75$ sample. The decrease of magnetic entropy change with increasing Ce content may be attributed to the decrease of the saturation magnetization.

Acknowledgements

This work was supported by the Inonu University research fund with the project number 2011/143.

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