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Phase transitions and magnetocaloric and transport properties in off-stoichiometric GdNi$_2$Mn$_x$

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The structural, magnetic, magnetocaloric, transport, and magneto-resistance properties of the rare-earth intermetallic compounds GdNi$_2$Mn$_x$ ($0.5 \leq x \leq 1.5$) have been studied. The compounds with $x = 0.5$ and 0.6 crystallize in the cubic MgCu$_2$ type phase, whereas samples with $x \geq 0.8$ form a mixed MgCu$_2$ and rhombohedral PuNi$_3$ phase. A second order magnetic phase transition from a ferromagnetic to paramagnetic state was observed near the Curie temperature ($T_C$). The GdNi$_2$Mn$_x$ ($0.5 \leq x \leq 1.5$) compounds order in a ferrimagnetic structure in the ground state. The largest observed values of magnetic entropy changes (at $T_C$ for $AH = 5T$) were 3.9, 3.5, and 3.1 J/Kg K for $x = 0.5$, 0.6, and 0.8, respectively. The respective relative values of the cooling power were 395, 483, and 220 J/kg. These values are greater than some well-known prototype magnetocaloric materials such as Gd (400 J/kg) and Gd$_2$Si$_2$Ge$_2$ (240 J/kg). Analysis of the resistivity data showed a $T^2$ dependence at low temperatures, suggesting strong electron-phonon interactions, whereas at higher temperatures s-d scattering was dominated by the electron-phonon contribution, resulting in a slow increase in resistivity. Magneto-resistance values of $\sim-1.1\%$ were found for $x = 0.5$ near $T_C$, and $-7\%$ for $x = 1.5$ near $T = 80\, \text{K}$. © 2016 AIP Publishing LLC.

I. INTRODUCTION

The study of rare-earth-3d transition-metal (R-T) intermetallic compounds has attracted attention in recent years because of potential multifunctional properties, such as high magneto-resistance (MR), large magnetostriction, and giant magnetocaloric effects (MCEs). $^{1-3}$ Intermetallic compounds of RT$_2$-type (with $T = \text{Ni, Mn, Co, and Fe}$) crystallize into a simple MgCu$_2$-type cubic Laves phase and are interesting because of the interplay between the localized 4f electrons and 3d itinerant electrons. $^{4,5}$

Wang et al. $^{6}$ synthesized and studied RNi$_2$Mn ($R = \text{Tb, Dy, Ho, and Er}$) compounds and found that they also crystallize in the cubic MgCu$_2$-type structure (space group Fd $3\, m$) in spite of a 1:3 R to T ratio. The Curie temperatures ($T_C$) of these compounds were found to be considerably lower than those of the RNi$_2$ and R Mn$_2$ compounds ($7$ to $45\, \text{K}$ range). The largest value of $T_C$ ($131\, \text{K}$) was observed in RNi$_2$Mn with $R = \text{Tb}$ as compared to $R = \text{Dy, Ho, and Er}$. $^{6}$

Gerasimov et al. $^{7}$ reported that off-stoichiometric GdNi$_2$Mn$_x$ ($0 < x < 0.4$) crystallizes in a cubic MgCu$_2$-type structure. Compounds with higher Mn concentrations ($x \geq 0.4$) form a mixed phase consisting of a cubic Laves (C15) and a rhombohedral PuNi$_3$-type structure (space group R $3\, m$). The Curie temperature $T_C$ was found to increase with increasing Mn concentration and was much greater ($T_C = 190\, \text{K}$ for $x = 0.4$) than that observed in Ref. 6 for $R = \text{Tb}$ ($T_C = 131\, \text{K}$). The magnetization measurements showed that GdNi$_2$Mn$_x$ forms in a ferrimagnetic structure in the ground state. $^{7}$ In the present work, we analyze the phase transition and report the transport properties and MCEs in single and multiphase GdNi$_2$Mn$_x$ with $0.5 \leq x \leq 1.5$.

II. EXPERIMENTAL TECHNIQUES

Bulk off-stoichiometric polycrystalline samples (3 g) of GdNi$_2$Mn$_x$ ($x = 0.5, 0.6, 0.8, 1.2, 1.4, \text{and } 1.5$) were prepared by arc-melting the constituent elements of purity better than 99.99% under a constant flow of ultra-high purity argon. The compounds were annealed in high vacuum ($\sim 10^{-5}\, \text{Torr}$) for 96 hours at $860\, ^\circ\text{C}$. An X-ray diffractometer with CuK$_\alpha$ radiation was used to measure the room temperature X-ray diffraction (XRD) patterns. Magnetization and resistivity were measured in a temperature interval of $5$ to $380\, \text{K}$ in magnetic fields up to $5\, \text{T}$ using a superconducting quantum interference device magnetometer (SQUID by Quantum Design) and by the four-probe method, respectively.

III. RESULT AND DISCUSSION

The room temperature X-ray diffraction patterns of GdNi$_2$Mn$_x$ compounds ($0.5 \leq x \leq 1.5$) are shown in Figure 1. The XRD patterns for the compounds with $x = 0.5$ and 0.6 show clear evidence of a cubic MgCu$_2$-type Laves phase, (C15). For samples with $x = 0.8$ and higher, a mixed phase of cubic MgCu$_2$-type and rhombohedral PuNi$_3$-type was observed. As the Mn concentration increases, the volume of the PuNi$_3$-type phase increases. The estimated percent of secondary phase (PuNi$_3$-type) is shown in Figure 1. The XRD peaks for the cubic MgCu$_2$-type and rhombohedral PuNi$_3$-type phases were indexed in Figures 1(a) and 1(e), respectively. $^{8,9}$ The values of the cell parameters were determined by fitting the XRD data (see Table 1 for the cubic and Figure 1(e) for the rhombohedral structures, respectively). The Mn atoms have a larger or smaller metallic radius...


(r = 0.137 nm) compared to that of Ni (r = 0.125 nm) and Gd (0.1804 nm), respectively. As one can see in Table I, the cell parameter increases with increasing Mn concentration. Therefore, Mn must be occupying the Ni site. The calculated values of the lattice parameters for the cubic phase were in good agreement with those reported in previous studies to within 1% (for x = 0.5) and 1.1% (for x = 0.6).

Figure 2 shows the field dependence of the magnetization M(H) measured at T = 5 K. The saturation magnetization decreased with increasing Mn concentration, consistent with results reported in Ref. 7. The saturation magnetization for GdNi2Mnx compounds ranging from x = 0.5 to 1.5 was much smaller than the gJμB = 7μB for Gd3⁺ ions. This indicates that GdNi2Mnx most likely forms a ferrimagnetic structure, with the magnetic moments of Gd being ordered antiparallel to the Mn-Ni 3d subsystem. The value of the magnetic moment of the Mn-Ni 3d subsystem was estimated from the magnetization data (Fig. 2) assuming a collinear antiparallel ordering of the magnetic moment of Gd (μGd) and the Mn-Ni subsystem (μMn-Ni) as

\[ μ(\text{Mn-Ni}) = μ_{\text{Gd}} - μ, \]

where μ is the experimentally measured magnetic moment per formula unit of the GdNi2Mnx compound and μGd = 7μB is the magnetic moment of free Gd3⁺ ions in the ground state. The estimated magnetic moment values for different Mn concentrations are listed in Table I. The increase in the magnetic moment of the 3d system can be interpreted under the assumption that the Mn atoms carry a large magnetic moment while the Ni atoms have a negligible contribution.

The temperature dependence of magnetization, M(T), measured at H = 100 Oe for GdNi2Mnx during heating is shown in Figure 3. All samples show ferromagnetic (FM) nature below the Tc. A second order magnetic phase transition (SOT) from a ferromagnetic to paramagnetic (PM) state was observed at Tc in these compounds. The Curie temperature, obtained from the minimum in dM/dT in the M(T) curve, was found to increase with increasing Mn concentration. According to Ref. 7, the Curie temperature of GdNi2 is 80 K. When Mn is added, Tc increases sharply and reaches a maximum value of ~202 K for x = 0.6 and decreases for higher Mn concentrations. The increase in the Curie temperature with Mn content is likely due to an enhancement of the T-T and R-T exchange interactions resulting from the increase in the magnetic moment of the 3d subsystem. At large Mn concentrations, the decrease in Tc could be due to a misorientation of magnetic moments in the R sublattice.

<table>
<thead>
<tr>
<th>Mn concentration (x)</th>
<th>a (Å)</th>
<th>Tc/Tc Arrott (K/K)</th>
<th>μ(\text{Mn-Ni}) (μB/μu)</th>
<th>−ΔS_m (J/kg K)</th>
<th>RCP (J/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>7.127</td>
<td>179/173</td>
<td>1.50</td>
<td>3.9</td>
<td>395</td>
</tr>
<tr>
<td>0.6</td>
<td>7.119</td>
<td>202/178</td>
<td>2.10</td>
<td>3.5</td>
<td>483</td>
</tr>
<tr>
<td>0.8</td>
<td>7.140</td>
<td>157/162</td>
<td>2.80</td>
<td>3.1</td>
<td>220</td>
</tr>
<tr>
<td>1.2</td>
<td>7.136</td>
<td>182/181</td>
<td>2.30</td>
<td>2.8</td>
<td>201</td>
</tr>
<tr>
<td>1.4</td>
<td>7.124</td>
<td>179/181</td>
<td>2.28</td>
<td>2.9</td>
<td>208</td>
</tr>
<tr>
<td>1.5</td>
<td>7.126</td>
<td>165/168.5</td>
<td>3.20</td>
<td>2.5</td>
<td>172</td>
</tr>
</tbody>
</table>

FIG. 1. Room temperature XRD patterns of GdNi2Mnx (x = 0.5, 0.6, 0.8, 1.2, and 1.5). The peaks for cubic MgCu2-type and rhombohedral PuNi3-type phases are indexed in Figures 1(a) and 1(e), respectively. The calculated values of lattice parameters for the rhombohedral PuNi3-type phase are shown in Figure 1(e).

FIG. 2. M(H) curves of GdNi2Mnx for different concentrations (x) measured at T = 5 K with change in field (H) up to 5 T.
In order to determine the type and order of the magnetic transitions, Arrott plots of $M^2$ versus $H/M$ were plotted (see Figure 4). The positive slopes of the Arrott plots indicate the FM to PM transitions are of second order (SOT).\textsuperscript{12} The values of $T_C$ calculated from the Arrott plots are in good agreement with those obtained from the minimum in $dM/dT$ in the $M(T)$ curves (see Table I).

The magnetic entropy changes ($-\Delta S_M$) in the vicinity of $T_C$ for different magnetic fields ($\Delta H$) are shown in Figure 5. The $-\Delta S_M$ were calculated using the Maxwell relation, $(\partial S/\partial H)_T = (\partial M/\partial T)_H$, from magnetization isotherms measured at different temperatures.\textsuperscript{3} The measured values of $-\Delta S_M$ for GdNi$_2$Mn$_x$ (0.5 $\leq$ $x$ $\leq$ 1.5) compounds near $T_C$ in an applied field $\Delta H$ = 5 T are summarized in Table I. From the table, it can be seen that the decrease in the value of $-\Delta S_M$ with increasing Mn concentration is related to the presence of second phase. Compounds with $x$ = 0.5, 0.6, and 0.8 exhibit large values of $-\Delta S_M$ = 3.9, 3.5, and 3.1 J/kg K, respectively. These values are greater than the values obtained in GdNi$_2$Mn$_x$ ($x \leq 0.4$) and TbNi$_2$Mn compounds.\textsuperscript{7,8} The large values of $-\Delta S_M$ near $T_C$ are due to jump-like changes in the magnetization from a FM ordered phase to a PM disordered phase, corresponding to SOTs which are evident in the M(T) curves (Figure 3). It is also interesting to note that $-\Delta S_M(T)$ spanned a wide temperature range. Such table-top-like MCE properties are important for practical applications.

The relative cooling power (RCP) is an important parameter that estimates the usefulness of a material as a magnetic refrigerant and can be used to compare different materials. The RCP is a measure of the amount of heat transferred between the hot and cold reservoirs in an ideal refrigeration cycle and is defined as $\text{RCP} = -\Delta S_M \times \Delta T$, where $\Delta T$ is the full width at half maximum of the $-\Delta S_M$ curve.\textsuperscript{13} Large values of the RCP = 395, 483, and 220 J/kg were found corresponding to the compounds with $x$ = 0.5, 0.6, and 0.8, respectively, with $\Delta H$ = 5 T. Some of the values obtained are greater than or comparable to the best prototype magnetocaloric materials such as Gd (400 J/kg)\textsuperscript{3} and Gd$_5$Si$_2$Ge$_2$ (240 J/kg).\textsuperscript{14} Due to the lower rare-earth element content and large RCP over a wide temperature range, these compounds can be considered as promising candidates for magnetic refrigeration.

For magnetic materials with a second order phase transition, mean-field theory predicts that the value of the isothermal magnetic entropy change $-\Delta S_M$ near $T_C$ is related to the field according to the relation$\textsuperscript{15}$

**FIG. 3.** The temperature dependence of magnetization $M(T)$ curves for GdNi$_2$Mn$_x$ ($x$ = 0.5, 0.6, 0.8, 1.2, 1.4, and 1.5) on heating in an applied magnetic field of $H$ = 100 Oe.

**FIG. 4.** The Arrott plots of $M^2$ versus $H/M$ in GdNi$_2$Mn$_x$ for $x$ = 0.8, 1.2, 1.4, and 1.5 with $\Delta T$ = 10 K.
The linear fit to the data in Figure 6 clearly shows that the relationship (2) is valid for GdNi$_2$Mn$_x$ compounds near $T_C$. This is further evidence that the transitions are of second order.

The contributions to the total electrical resistivity, $\rho(T)$, from electron–phonon interactions ($\rho_{ph}(T)$), magnetic scattering ($\rho_{mag}(T)$), and the residual resistivity ($\rho_o$) have been determined. According to the Matthiessen’s rule, the total temperature dependence of the resistivity can be written as

$$\rho(T) = \rho_o + \rho_{ph}(T) + \rho_{mag}(T).$$

Depending on the temperature range, either $\rho_{ph}(T)$ or $\rho_{mag}(T)$ dominates. Typical $\rho(T)$ and MR curves for the compounds $x = 0.5$ and $1.5$ are shown in Figures 7 and 8, respectively. At higher temperature, the compounds show a slowly increasing $\rho(T)$ curve. Similar $\rho(T)$ behavior has been observed in Ref. 16. In the temperature interval $T \gg T_C$, $\rho_{mag}(T)$ is considered to be temperature independent and the changes in the total resistivity are due to $\rho_{ph}(T)$. Below $T_C$, $\rho_{mag}(T)$ undergoes a sharp, continuous decrease that dominates over the linear decrease in $\rho_{ph}(T)$. This results in an overall decrease in $\rho(T)$ below $T_C$.

At low temperatures, $\rho(T)$ follows a $T^2$ law according to $\rho(T) = \rho_o + AT^2$, which suggests a dominant electron–electron interaction.
scattering behavior.\textsuperscript{17} The value of the constant $A = 3.2$ $\text{m$\Omega cm/K^2}$ was determined from a linear fit of the $\rho(T)$ data for $x = 0.5$ (see inset (a) of Fig. 7). The residual resistivity ($\rho_0$) was calculated to be 0.19 $\text{m$\Omega cm}$ and 0.06 $\text{m$\Omega cm}$ for $x = 0.5$ and 1.5, respectively. Using relation (3), the $\rho_{mag}$ (constant) contributions to the total resistivity were calculated to be 0.02 and 0.15 $\text{m$\Omega cm}$ for $x = 0.5$ and $x = 1.5$, respectively, by extrapolation of $\rho(T)$ to $T = 0$ from the high temperature region ($T > 200 \text{K}$). The magnetoresistance (MR) was calculated to be 0.02 and 0.15 $\text{m$\Omega cm}$ for $x = 0.5$ and $x = 1.5$, respectively, by extrapolation of $\rho(T)$ to $T = 0$ from the high temperature region ($T > 200 \text{K}$). The percent change in the MR was $\sim -1.1\%$ for $x = 0.5$ near $T_C$, and $-7\%$ for $x = 1.5$ near $T = 80 \text{K}$.

IV. CONCLUSIONS

The crystal structures, magnetic phase transitions, magnetocaloric, and transport properties in off-stoichiometric GdNi$_2$Mn$_x$ ($0.5 \leq x \leq 1.5$) compounds were investigated. The experimental results showed that the compounds with $x = 0.5$ and 0.6 crystallize in a cubic MgCu$_2$-type phase, whereas those with $x \geq 0.8$ form a mixed MgCu$_2$-type and rhombohedral PuNi$_3$-type phase. The cell parameters for the cubic phase were found to increase with increasing Mn concentration. A second order magnetic transition from a FM to PM phase was observed. The $T_C$ increased for lower Mn concentrations, reaching a maximum value of 202 K at $x = 0.6$, and decreased for higher Mn contents. The saturation magnetic moment values of GdNi$_2$Mn$_x$ indicate a ferrimagnetic ground state, with the magnetic moments of Gd ordered antiparallel to the Mn-Ni 3d subsystem. Large values of $-\Delta S_M$ and RCP for $\Delta H = 5 \text{T}$ were found in the compounds with $x \geq 0.5$, which is important for cooling applications. The resistivity, $\rho(T)$, showed a $T^2$ dependence at low temperature, suggesting strong electron-electron interactions. At high temperature, $\rho_{mag}(T)$ due to s-d scattering was dominated by electron-phonon scattering, resulting in a slow increase in the resistivity. Magnetoresistance values of $\Delta \rho \sim -1.1\%$ and $-7\%$ were found for $x = 0.5$ near $T_C$ and for $x = 1.5$ near $T = 80 \text{K}$, respectively.

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