1-28-2016

Phase transitions and magnetocaloric and transport properties in off-stoichiometric GdNi₂Mnx

Anil Aryal
Southern Illinois University Carbondale

Abdiel Quetz
Southern Illinois University Carbondale

Sudip Pandey
Southern Illinois University Carbondale

Tapas Samanta
Louisiana State University

Igor Dubenko
Southern Illinois University Carbondale

See next page for additional authors

Follow this and additional works at: https://digitalcommons.lsu.edu/physics_astronomy_pubs

Recommended Citation

Aryal, A., Quetz, A., Pandey, S., Samanta, T., Dubenko, I., Mazumdar, D., Stadler, S., & Ali, N. (2016). Phase transitions and magnetocaloric and transport properties in off-stoichiometric GdNi₂Mnx. *Journal of Applied Physics*, 119 (4) <https://doi.org/10.1063/1.4940877>

This Article is brought to you for free and open access by the Department of Physics & Astronomy at LSU Digital Commons. It has been accepted for inclusion in Faculty Publications by an authorized administrator of LSU Digital Commons. For more information, please contact ir@lsu.edu.

Authors

Anil Aryal, Abdiel Quetz, Sudip Pandey, Tapas Samanta, Igor Dubenko, Dipanjan Mazumdar, Shane Stadler, and Naushad Ali

Phase transitions and magnetocaloric and transport properties in off-stoichiometric GdNi_2Mn_x

Cite as: J. Appl. Phys. **119**, 043905 (2016); <https://doi.org/10.1063/1.4940877>

Submitted: 23 November 2015 • Accepted: 15 January 2016 • Published Online: 28 January 2016

Anil Aryal, Abdiel Quetz, Sudip Pandey, et al.

View Online

Export Citation

CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Giant magnetocaloric effect in antiferromagnetic \$\text{ErRu}_2\text{Si}_2\$ compound](#)

Applied Physics Letters **91**, 152506 (2007); <https://doi.org/10.1063/1.2798594>

[Field dependence of the magnetocaloric effect in materials with a second order phase transition: A master curve for the magnetic entropy change](#)

Applied Physics Letters **89**, 222512 (2006); <https://doi.org/10.1063/1.2399361>

[Giant magnetocaloric effect of \$\text{MnAs}_{1-x}\text{Sb}_x\$](#)

Applied Physics Letters **79**, 3302 (2001); <https://doi.org/10.1063/1.1419048>

Applied Physics
Reviews

Read. Cite. Publish. Repeat.

19.162

2020 IMPACT FACTOR*

Phase transitions and magnetocaloric and transport properties in off-stoichiometric GdNi_2Mn_x

Anil Aryal,¹ Abdiel Quetz,¹ Sudip Pandey,¹ Tapas Samanta,² Igor Dubenko,¹ Dipanjan Mazumdar,¹ Shane Stadler,² and Naushad Ali¹

¹Department of Physics, Southern Illinois University, Carbondale, Illinois 62901, USA

²Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803, USA

(Received 23 November 2015; accepted 15 January 2016; published online 28 January 2016)

The structural, magnetic, magnetocaloric, transport, and magnetoresistance properties of the rare-earth intermetallic compounds GdNi_2Mn_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_2Mn_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 $\Delta H = 5\text{ T}$) 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 $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (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. Magnetoresistance 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.

[<http://dx.doi.org/10.1063/1.4940877>]

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 magnetoresistance (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_2Mn ($R = \text{Tb, Dy, Ho, and Er}$) compounds and found that they also crystallize in the cubic MgCu_2 -type structure (space group $\text{Fd } \bar{3} \text{ m}$) in spite of a 1:3 R to T ratio. The Curie temperatures (T_C) of these compounds were found to be considerably larger than those of the RNi_2 and RMn_2 compounds (7 to 45 K range). The largest value of T_C (131 K) was observed in RNi_2Mn with $R = \text{Tb}$ as compared to $R = \text{Dy, Ho, and Er}$.

Gerasimov *et al.*⁷ reported that off-stoichiometric GdNi_2Mn_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 $R \bar{3} \text{ m}$). 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_2Mn_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_2Mn_x with $0.5 \leq x \leq 1.5$.

II. EXPERIMENTAL TECHNIQUES

Bulk off-stoichiometric polycrystalline samples (3 g) of GdNi_2Mn_x ($x = 0.5, 0.6, 0.8, 1.2, 1.4$, 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 ($\approx 10^{-5}$ Torr) for 96 h at 860°C . An X-ray diffractometer with $\text{CuK}\alpha$ 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 K in magnetic fields up to 5 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_2Mn_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 I for the cubic and Figure 1(e) for the rhombohedral structures, respectively). The Mn atoms have a larger or smaller metallic radius

FIG. 1. Room temperature XRD patterns of GdNi_2Mn_x ($x = 0.5, 0.6, 0.8, 1.2$, and 1.5). The peaks for cubic MgCu_2 -type and rhombohedral PuNi_3 -type phases are indexed in Figures 1(a) and 1(e), respectively. The calculated values of lattice parameters for the rhombohedral PuNi_3 -type phase are shown in Figure 1(e).

($r = 0.137$ 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.^{7,10} 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 $x = 0.6$).⁷

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 GdNi_2Mn_x compounds ranging from $x = 0.5$ to 1.5 was much smaller than the $gJ\mu_B = 7\mu_B$ for Gd^{3+} ions. This indicates that GdNi_2Mn_x 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

FIG. 2. $M(H)$ curves of GdNi_2Mn_x for different concentrations (x) measured at $T = 5$ K with change in field (H) up to 5 T.

from the magnetization data (Fig. 2) assuming a collinear antiparallel ordering of the magnetic moment of Gd (μ_{Gd}) and the Mn-Ni subsystem ($\mu_{\text{Mn-Ni}}$) as

$$\mu_{(\text{Mn-Ni})} = \mu_{\text{Gd}} - \mu, \quad (1)$$

where μ is the experimentally measured magnetic moment per formula unit of the GdNi_2Mn_x compound and $\mu_{\text{Gd}} = 7\mu_B$ is the magnetic moment of free Gd^{3+} 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.⁶

The temperature dependence of magnetization, $M(T)$, measured at $H = 100$ Oe for GdNi_2Mn_x during heating is shown in Figure 3. All samples show ferromagnetic (FM) nature below the T_C . A second order magnetic phase transition (SOT) from a ferromagnetic to paramagnetic (PM) state was observed at T_C 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 GdNi_2 is 80 K. When Mn is added, T_C 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 T_C could be due to a misorientation of magnetic moments in the R sublattice.¹¹

TABLE I. Cell parameters (cubic), Curie temperature, magnetic moment, magnetic entropy change, and relative cooling power of GdNi_2Mn_x compound.

Mn concentration (x)	a (Å)	$T_C/T_{C(\text{Arrott})}$ (K/K)	$\mu_{(\text{Mn-Ni})}$ ($\mu_B/\text{f.u.}$)	$-\Delta S_M$ (J/kg K)	RCP (J/kg)
0.5	7.127	179/173	1.50	3.9	395
0.6	7.119	202/178	2.10	3.5	483
0.8	7.140	157/162	2.80	3.1	220
1.2	7.136	182/181	2.30	2.8	201
1.4	7.124	179/181	2.28	2.9	208
1.5	7.126	165/168.5	3.20	2.5	172

FIG. 3. The temperature dependence of magnetization $M(T)$ curves for GdNi_2Mn_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.

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).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 (ΔH) 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.³ The measured values of $-\Delta S_M$ for GdNi_2Mn_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_2Mn_x ($x \leq 0.4$) and TbNi_2Mn compounds.^{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 ΔT is the full width at half maximum of the $-\Delta S_M$ curve.¹³ Large values of the $\text{RCP} = 395, 483$, 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)³ and $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (240 J/kg).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 relation¹⁵

FIG. 4. The Arrott plots of M^2 versus H/M in GdNi_2Mn_x for $x = 0.8, 1.2, 1.4$, and 1.5 with $\Delta T = 10$ K.

FIG. 5. Magnetic entropy changes ($-\Delta S_M$) as a function of temperature for GdNi_2Mn_x at different values of magnetic field change (ΔH) near T_C .

$$|\Delta S_M| \propto H^{2/3}. \quad (2)$$

The linear fit to the data in Figure 6 clearly shows that the relationship (2) is valid for GdNi_2Mn_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 ($\rho_{\text{ph}}(T)$), magnetic scattering ($\rho_{\text{mag}}(T)$), and the residual resistivity (ρ_o) have been determined. According to the Matthiessen's rule, the total temperature dependence of the resistivity can be written as

$$\rho(T) = \rho_o + \rho_{\text{ph}}(T) + \rho_{\text{mag}}(T). \quad (3)$$

Depending on the temperature range, either $\rho_{\text{ph}}(T)$ or $\rho_{\text{mag}}(T)$ 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 $T \gg T_C$, $\rho_{\text{mag}}(T)$ is considered to be temperature independent and the changes in the total resistivity are due to $\rho_{\text{ph}}(T)$. Below T_C , $\rho_{\text{mag}}(T)$ undergoes a sharp, continuous decrease that dominates over the linear decrease in $\rho_{\text{ph}}(T)$. 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

FIG. 6. Dependence of the magnetic entropy changes ($-\Delta S_M$) on $H^{2/3}$ for GdNi_2Mn_x near T_C .

FIG. 7. The $\rho(T)$ curve for $x=0.5$ at $H=0$ T and 5 T. Inset (a) the fit of the zero-field data by $\rho(T) = \rho_o + AT^2$ in the temperature range 10–23 K; Inset (b) magnetoresistance as a function of temperature for $H=5$ T.

FIG. 8. The $\rho(T)$ curve for $x = 1.5$ at $H = 0$ T and 5 T. Inset (b) magnetoresistance as a function of temperature for $H = 5$ T.

scattering behavior.¹⁷ The value of the constant $A = 3.2 \text{ n}\Omega \text{ cm/K}^2$ was determined from a linear fit of the $\rho(T)$ data for $x = 0.5$ (see inset (a) of Fig. 7). The residual resistivity (ρ_0) was calculated to be $0.19 \text{ m}\Omega \text{ cm}$ and $0.06 \text{ m}\Omega \text{ cm}$ for $x = 0.5$ and 1.5 , respectively. Using relation (3), the ρ_{mag} (constant) contributions to the total resistivity were calculated to be 0.02 and $0.15 \text{ m}\Omega \text{ cm}$ 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 using the standard definition $(\Delta\rho/\rho_0) \times 100\%$, where $\Delta\rho = [\rho(H = 5 \text{ T}, T) - \rho_0]$ and $\rho_0 = \rho(H = 0, T)$. 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_2Mn_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_2Mn_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, $\rho_{\text{mag}}(T)$ 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.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award Nos. DE-FG02-06ER46291 and DE-FG02-13ER46946.

- ¹R. Nirmala, Ya. Mudryk, V. K. Pecharsky, and K. A. Gschneidner, Jr., *Phys. Rev. B* **76**, 014407 (2007).
- ²G. Engdahl, *Handbook of Giant Magnetostrictive Materials* (Academic Press, USA, 2000).
- ³K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).
- ⁴K. H. J. Buschow, *Rep. Prog. Phys.* **40**, 1179–1256 (1977).
- ⁵E. Gratz and A. S. Markosyan, *J. Phys.: Condens. Matter* **13**, R385–R413 (2001).
- ⁶J. L. Wang, C. Marquina, M. R. Ibarra, and G. H. Wu, *Phys. Rev. B* **73**, 094436 (2006).
- ⁷E. G. Gerasimov, N. V. Mushnikov, P. B. Terentev, V. S. Gaviko, and A. A. Inishev, *J. Alloys Compd.* **571**, 132–137 (2013).
- ⁸J. L. Wang, S. J. Campbell, S. J. Kennedy, R. Zeng, S. X. Dou, and G. H. Wu, *J. Phys.: Condens. Matter* **23**, 216002 (2011).
- ⁹K. Younsi, V. Russier, L. Bessais, and J.-C. Crivello, *J. Phys.: Conf. Ser.* **303**, 012028 (2011).
- ¹⁰F. Stein, M. Palm, and G. Sauthoff, *Intermetallics* **12**, 713 (2004).
- ¹¹N. V. Mushnikov, V. S. Gaviko, E. G. Gerasimov, P. B. Terent'ev, and I. A. Tkach, *Phys. Metals and Metallography* **110**, 210 (2010).
- ¹²A. Arrott, *Phys. Rev.* **108**, 1394 (1957).
- ¹³A. M. Tishin and Y. I. Spichkin, *The Magnetocaloric Effect and its Applications* (IOP Publishing Ltd., 2003).
- ¹⁴V. Provenzano, A. J. Shapiro, and R. D. Shull, *Nature (London)* **429**, 853 (2004).
- ¹⁵H. Oesterreicher and F. T. Parker, *J. Appl. Phys.* **55**, 4334 (1984).
- ¹⁶E. Gratz and M. J. Zukermann, *J. Magn. Magn. Mater.* **29**, 181–191 (1982).
- ¹⁷T. Samanta, I. Dubenko, A. Quetz, J. Prestigiacomo, P. W. Adams, S. Stadler, and N. Ali, *Appl. Phys. Lett.* **103**, 042408 (2013).