2011

Magnetic phase transition and Mossbauer spectroscopy of ErNi₂Mnx compounds

Jianli Wang

University of Wollongong, jianli@uow.edu.au

S J. Campbell

UNSW, stewart.campbell@adfa.edu.au

R Zeng

University of Wollongong, rzeng@uow.edu.au

S. X. Dou

University of Wollongong, shi@uow.edu.au

S J. Kennedy

Bragg Institute ANSTO Australia

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>

Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/1372>

Recommended Citation

Wang, Jianli; Campbell, S J.; Zeng, R; Dou, S. X.; and Kennedy, S J.: Magnetic phase transition and Mossbauer spectroscopy of ErNi₂Mnx compounds 2011.
<https://ro.uow.edu.au/engpapers/1372>

Magnetic phase transition and Mössbauer spectroscopy of ErNi_2Mn_x compounds

J. L. Wang, S. J. Campbell, R. Zeng, S. X. Dou, and S. J. Kennedy

Citation: *J. Appl. Phys.* **109**, 07E304 (2011); doi: 10.1063/1.3535544

View online: <http://dx.doi.org/10.1063/1.3535544>

View Table of Contents: <http://jap.aip.org/resource/1/JAPIAU/v109/i7>

Published by the [American Institute of Physics](#).

Related Articles

Self-similarity in $(\partial M/\partial T)H$ curves for magnetocaloric materials with ferro-to-paramagnetic phase transitions
J. Appl. Phys. **111**, 07A950 (2012)

Electrical control of Curie temperature in cobalt using an ionic liquid film
Appl. Phys. Lett. **100**, 122402 (2012)

Investigation of spin and orbital moments of L10 FePtRh thin films
J. Appl. Phys. **111**, 07C120 (2012)

Comparison of magnetic and thermoelectric properties of $(\text{Nd,Ca})\text{BaCo}_2\text{O}_{5.5}$ and $(\text{Nd,Ca})\text{CoO}_3$
J. Appl. Phys. **111**, 07D727 (2012)

Size-dependent ferromagnetic phase transition in $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ nanoparticles
J. Appl. Phys. **111**, 056104 (2012)

Additional information on *J. Appl. Phys.*

Journal Homepage: <http://jap.aip.org/>

Journal Information: http://jap.aip.org/about/about_the_journal

Top downloads: http://jap.aip.org/features/most_downloaded

Information for Authors: <http://jap.aip.org/authors>

ADVERTISEMENT

**FIND THE NEEDLE IN THE
HIRING HAYSTACK**

Post jobs and reach
thousands of hard-to-find
scientists with specific skills

<http://careers.physicstoday.org/post.cfm> **physicstoday JOBS**

Magnetic phase transition and Mössbauer spectroscopy of ErNi_2Mn_x compounds

J. L. Wang,^{1,2,a)} S. J. Campbell,¹ R. Zeng,³ S. X. Dou,³ and S. J. Kennedy²¹*School of Physical, Environmental and Mathematical Sciences, The University of New South Wales, The Australian Defence Force Academy, Canberra ACT 2600, Australia*²*Bragg Institute, ANSTO, Lucas Heights, NSW 2234, Australia*³*Institute for Superconductivity and Electronic Materials, University of Wollongong, Australia*

(Presented 18 November 2010; received 21 September 2010; accepted 19 October 2010; published online 18 March 2011)

Investigation of ErNi_2Mn_x with $0.90 \leq x \leq 1.10$ indicates that the MgCu_2 -type structure (with space group $Fd-3m$) is formed within $x = 0.97-1.10$. Curie temperature $T_C = 50$ K of ErNi_2Mn is significantly higher than those of the corresponding ErNi_2 ($T_C = 7$ K) and ErMn_2 ($T_C = 15$ K) compounds. Detailed analyses of DC magnetization data demonstrate that the magnetic phase transition at the Curie temperature is second order. The magnetic entropy change around T_C has been found to be 4.8 J/kg K for a magnetic field change of 0 to 5 T with its relative cooling power ~ 283 J/kg. ^{57}Fe Mössbauer spectra below T_C have been fitted with three sub-spectra representing three inequivalent local magnetic environments while the paramagnetic spectra are fitted using two sub-spectra for two inequivalent crystal sites (8a and 16d), which supports the conclusion based on Rietveld refinement that Mn atoms occupy at both 8a and 16d sites. © 2011 American Institute of Physics. [doi:10.1063/1.3535544]

Recently, we found that the RNi_2Mn alloys with $\text{R} = \text{Tb}$, Dy, Ho, and Er crystallize in the unexpected MgCu_2 -type structure with their Curie temperatures being considerably higher than the T_C values of the corresponding RNi_2 and RMn_2 compounds.¹ Jackson *et al.*² and Mushnikov *et al.*³ confirmed our discovery¹ that TbNi_2Mn is a cubic Laves material even though Mushnikov *et al.* suggested that the subgroup $F4-3m$ may be more adequate than $Fd-3m$ to describe the crystal structure of TbNi_2Mn based on the appearance of the weak (200) and (420) reflections in their x-ray diffraction and neutron study on their sample. However, we did not observe these two specific reflections in our previous¹ and recent TbNi_2Mn_x samples.⁴ Such differences in the space group for TbNi_2Mn indicate that the structural and magnetic properties of RNi_2Mn compounds may be ultra sensitive to sample synthesis and heat-treatment conditions,¹⁻⁴ similar to the case in RNi_2 systems.⁵

Quite recently, Maji *et al.*⁶ reported that the RCo_2Mn ($\text{R} = \text{Ho}$ and Er) alloys also crystallize in the cubic MgCu_2 -type. Moreover, many attempts have been made to use experimental and theoretical atomic parameters to construct structural maps for various MgCu_2 -type ($Fd-3m$ space group) compounds owing to their relatively simple crystal structure and outstanding magnetic properties.^{7-9,9}

In this paper, we firstly address the effects of Mn content on structural properties in the ErNi_2Mn_x system in order to check the homogeneity range of ErNi_2Mn_x compounds with the MgCu_2 -type structure. Then we carry out a thorough investigation of the magnetic phase transition at T_C in ErNi_2Mn using variable temperature DC magnetization (5–340 K) and Mössbauer spectroscopy (5–300 K) measurements.

Ingots of ErNi_2Mn_x ($x = 0.90, 0.97, 1.00, 1.03$ and 1.10) were prepared by standard argon arc-melting the mixtures of

starting elements (purities $\geq 99.9\%$). The $\text{ErNi}_2\text{Mn}(^{57}\text{Fe})$ sample for the Mössbauer study was prepared from an ingot doped with ~ 0.5 wt% ^{57}Fe . All samples were characterized by x-ray diffraction ($\text{CuK}\alpha$ radiation; $\lambda = 1.5418$ Å). The neutron diffraction pattern of ErNi_2Mn was obtained using, Wombat ($\lambda = 2.4072$ Å) of OPAL, ANSTO. The ^{57}Fe Mössbauer spectra were obtained between 5 K and 300 K using a standard constant-acceleration spectrometer and a Rh^{57}Co source.

Typical x-ray diffraction (XRD) patterns at room temperature for ErNi_2Mn_x samples ($x = 0.97, 1.00$ and 1.10) are shown

FIG. 1. (Color online) (a) X-ray diffraction patterns at room temperature for ErNi_2Mn_x compounds with $x = 0.97, 1.00$ and 1.10 , (b) neutron diffraction pattern for ErNi_2Mn , and (c) composition dependence of lattice constant a for ErNi_2Mn_x compounds at room temperature.

^{a)}Electronic mail: wjlzzh@hotmail.com.

FIG. 2. (Color online) Temperature dependencies of dc magnetization of ErNi_2Mn measured in an applied field of ($\mu_0 H = 0.005$ T) under ZFC, FCC, and FCW conditions. The inset shows the temperature dependence of the inverse susceptibility ($\mu_0 H/M$).

in Fig. 1(a); the red lines represent the profiles calculated using the Le Bail fitting method. The XRD patterns of ErNi_2Mn_x samples with $x = 0.97-1.10$ can be well indexed using the space group $Fd-3m$. Moreover, the neutron diffraction data for ErNi_2Mn sample [Fig. 1(b)] also confirms that the space group of ErNi_2Mn sample belongs to $Fd-3m$. It can be seen clearly from Fig. 1(a) that the corresponding (200) (nominal $2\theta_{(200)} \sim 25^\circ$) and (420) reflections (nominal $2\theta_{(420)} \sim 51.3^\circ$) which are related with the superstructure of the $F-43m$ space group³ are absent in our ErNi_2Mn_x compounds. The variations^{1,3} in the description of crystal structure of RNi_2Mn samples indicates that the crystal structures of RNi_2Mn compounds are very sensitive to the composition and sample preparation conditions. Similar case has been found in RNi_2 system⁵ where a temperature induced phase transition is detected from space

group $F-43m$ (lower temperature) to $Fd-3m$ (higher temperature). The best Rietveld refinement of XRD pattern for ErNi_2Mn compound has been obtained with the pattern factor (R_p), the weighted pattern factor (R_w) and the expected pattern factor (R_{exp}) being 8.9%, 11.4%, and 5.78%, respectively. Rietveld refinement indicates that in the ErNi_2Mn compound the 8a sites are not fully occupied by Er atoms (only 73.9%) while Mn atoms occupy approximately 21.4% with about 4.7% of the 8a sites being empty. By comparison the 16d sites are fully shared by the Ni (73.9%) and Mn (26.1%) atoms.^{1,4} Similarly in (Ref. 1), we can rewrite ErNi_2Mn as $(\text{Er}_{0.739}\square_{0.047}\text{Mn}_{0.214})_1(\text{Ni}_{0.739}\text{Mn}_{0.261})_2$ (here $\square$ stands for the vacancy) which indicates that around 10% transition metal atoms occupy at rare earth site (8a site) in ErNi_2Mn compound.

The lattice parameter a [shown in Fig. 1(c)] increases with Mn content from $x = 0.97$ to 1.03, but remains essentially unchanged from $x = 1.03$ to 1.1; this indicates that the composition of the Laves phase is the same for alloys with $x > 1.03$. A similar case exists in the Zr_xCo_2 system.¹⁰

The dc magnetization $M(T)$ of ErNi_2Mn measured as a function of temperature in a magnetic field of $\mu_0 H = 0.005$ T is shown in Fig. 2. The zero field-cooled magnetization curve ZFC-W was measured on warming in a field of $\mu_0 H = 0.005$ T after first cooling in zero field. The field-cooled cooling magnetization curve F-CC was measured on cooling from 300 K to 5 K in an applied field of $\mu_0 H = 0.005$ T with the field-cooled warming curve F-CW obtained on warming in a 0.005 T field after first cooling the sample in a magnetic field of 0.005 T and measuring the magnetization with $\mu_0 H = 0.005$ T on warming. It can be seen that while the FCC and FCW curves are almost identical over the entire temperature range, different thermomagnetic behavior is observed for the ZFC and FCC magnetisation curves of ErNi_2Mn below 40 K; this behavior indicates the presence of magneto-history effect due to narrow magnetic domain pinning.^{4,11} The transition temperature has been determined from M^2-T plots to be $T_C = 50(\pm 1)$ K which is significantly higher than those of the corresponding ErNi_2 ($T_C = 7$ K) and ErMn_2 ($T_C = 15$ K) compounds. The presence of Ni and Mn magnetic moments in RNi_2Mn leads to stronger R-T and T-T exchange interactions,^{1,3,4} resulting in the higher T_C values for the series of RNi_2Mn compounds compared with RNi_2 and RMn_2 . As is evident from the inset to Fig. 2, above T_C , the inverse susceptibility (H/M) of ErNi_2Mn follows Curie-Weiss behavior.

FIG. 3. (Color online) (a) Magnetization as a function of applied DC field ($\mu_0 H = 0-5$ T) for ErNi_2Mn around the Curie temperature T_C . (b) Arrot-plots of M^2 as a function of $\mu_0 H/M$ for the magnetization data of Fig. 6(a).

FIG. 4. (Color online) (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$ for ErNi_2Mn . The inset shows the dependence of the entropy change $-\Delta S_M(T, H)$ on the parameter $(\mu_0 H/T_C)^{2/3}$.

FIG. 5. (Color online) (a) ^{57}Fe Mössbauer spectra of $\text{ErNi}_2\text{Mn}(^{57}\text{Fe})$ over the temperature range 5–300 K. (b) Composition dependence of isomer shift values δ .

Typical M versus $\mu_0 H$ curves for ErNi_2Mn are shown in Fig. 3(a) for the magnetic region of interest (10–95 K) with the corresponding Arrott plots of M^2 versus $\mu_0 H/M$ shown in Fig. 3(b). The positive slopes in the isotherm Arrott plots indicate that the transition at T_C for ErNi_2Mn is second-order.

The isothermal entropy change, corresponding to a magnetic field change $\Delta\mu_0 H$ starting from a zero field to $\mu_0 H$, has been derived from the magnetization data based on the Maxwell thermodynamic relation.^{8,9} The change in magnetic entropy change $-\Delta S_M$ as a function of temperature is shown in Fig. 4. For a field change from 0 T to 5 T, the maximum $-\Delta S_M$ value is found to be $4.8 \text{ J kg}^{-1} \text{ K}^{-1}$ around T_C . By comparison, $-\Delta S_M = 5.8 \text{ J/mol K}$ ($\sim 20.4 \text{ J/kg K}$) for ErNi_2 .¹² The reduction of $-\Delta S_M$ in ErNi_2Mn compared with ErNi_2 may be related to the disorder of the local environments created by the presence of the mixing occupancy of Er and Mn and vacancies at the 8a site.¹ In addition to the above value of $-\Delta S_M$, the relative cooling power (RCP) is also evaluated to determine the cooling efficiency of a magnetocaloric material.^{8,12} The relative cooling power values of ErNi_2Mn for field changes of 0–1 T, 0–2 T, 0–3 T, 0–4 T and 0–5 T are 36.2 J/kg, 88.6 J/kg, 149.6 J/kg, 215.9 J/kg and 283.4 J/kg, respectively.

The insert to Fig. 4 shows a graph of $-\Delta S_M$ plotted as a function of $(\mu_0 H/T_C)^{2/3}$ for data in the region around the transition temperature T_C . Mean field theory predicts that $-\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ at a second-order phase transition. The linear fit to the data in the insert of Fig. 4 demonstrates that the relationship $-\Delta S_M \propto (\mu_0 H/T_C)^{2/3}$ is valid around T_C , which confirms that the magnetic phase transition around T_C belongs to second order as derived above [Fig. 3(b)].

Typical Mössbauer spectra for the ^{57}Fe -doped ErNi_2Mn sample at various temperatures are shown in Fig. 5(a). Based

on the assumption that Mn atoms occupy both 8a and 16d sites mentioned above, we have fitted the spectra for $\text{ErNi}_2\text{Mn}(^{57}\text{Fe})$ in the paramagnetic state above T_C with two sub-spectra as the dopant ^{57}Fe atoms are expected to enter both the 8a and 16d sites similar to Mn atoms. Examples of the fits and the sub-spectral components for $\text{ErNi}_2\text{Mn}(^{57}\text{Fe})$ are shown in Fig. 5(a). The fractional area of two sub-spectra is derived to be 10% and 90%, respectively. This confirmed our conclusion obtained above from Rietveld refinement that 10% of total transition metal atoms occupy 8a site.¹

The spectra for magnetically split spectra below T_C have been fitted using at least three sub-spectra even though only two inequivalent crystal sites. The fractional areas A of the three sextets (S1, S2, S3) shown as sub-spectra in the 5 K spectrum of Fig. 4 were found to be $A_1 \sim 43\%$, $A_2 \sim 44\%$ and $A_3 \sim 13\%$. For analysis of the present Mössbauer spectra below T_C , we assume that the linewidth and isomer shift are the same for all three sub-spectra with the magnetic hyperfine field and quadrupole interaction also allowed to vary.⁴ Figure 5 shows that magnetic spectra below T_C have broad lines indicating a distribution of hyperfine parameters, similar to the case in RMn_2 system.¹³ Based on the occupancy factors of Mn atoms for the 16d and 8a sites,¹ we assume that sextets S1 and S2 of combined fractional area $\sim 90\%$, correspond to the contribution from ^{57}Fe at 16d sites with the third sextet S3 representing ^{57}Fe located at the 8a site. $B_{\text{hf}1}$, $B_{\text{hf}2}$, $B_{\text{hf}3}$ and B_{hf} (average) are derived to be 14.9, 10.8, 4.4 and 11.8 T, respectively with quadrupole shift ε (average) = 0.029 mm/s and isomer shift $\delta = 0.015 \text{ mm/s}$ at 5 K. Similar behavior has been found for RMn_2 compounds ($R = \text{Tb, Dy, Ho}$) where two sub-spectra rather than a single sub-spectrum (even dopant ^{57}Fe atoms only enter the 16d site) are required¹³ where both the simultaneous presence of magnetic and nonmagnetic Mn atoms and the specific easy axis of magnetization in a given compound is found to lead to the occurrence of additional subspectra.¹³

The Debye temperature θ_D of $\text{ErNi}_2\text{Mn}(^{57}\text{Fe})$ has been determined to be $200 \pm 20 \text{ K}$ from the fitting the temperature dependence of the isomer shift $\delta(T)$ shown in the Fig. 5(b). By comparison, the θ_D for ErNi_2 was reported to be 264 K.¹⁴

This work is supported by a joint agreement between ANSTO and UNSW, and Australian Research Council.

¹J. L. Wang et al., *Solid State Commun.* **121**, 615 (2002); J. L. Wang et al., *Phys. Rev. B* **73**, 094436 (2006).

²D. D. Jackson et al., *Phys. Rev. B* **75**, 224422 (2007).

³N. V. Mushnikov et al., *Phys. Rev. B* **79**, 184419 (2009).

⁴J. L. Wang et al., "Magnetic transition in TbNi_2Mn —Magnetisation and Mössbauer spectroscopy," in preparation.

⁵E. Gratz et al., *J. Phys.: Condens. Matter* **11**, 7893 (1999); E. Gratz et al., *J. Phys.: Condens. Matter* **8**, 8351 (1996).

⁶B. Maji et al., *J. Magn. Magn. Mater.* **322**, 2415 (2010).

⁷G. Engdahl, *Handbook of Giant Magnetostrictive Materials* (Academic Press, New York, 2000).

⁸K. A. Gschneidner, Jr., V. K. Pecharsky, and A. O. Tsokol, *Rep. Prog. Phys.* **68**, 1479 (2005).

⁹M. Halder et al., *Phys. Rev. B* **81**, 174402 (2010).

¹⁰J. H. Zhu and C. T. Liu, *Acta Mater.* **48**, 2339 (2000).

¹¹J. L. Wang et al., *J. Appl. Phys.* **92**, 1453 (2002).

¹²P. J. von Ranke et al., *Phys. Rev. B* **63**, 184406 (2001).

¹³J. Marzec et al., *J. Magn. Magn. Mater.* **157–158**, 413 (1996).

¹⁴M. R. Ibarra et al., *J. Phys. Chem. Solid.* **45**, 789 (1984).