Accepted Manuscript

Collinear antiferromagnetic structure in R_2Ni_2In (R = Er, Tm)

S. Baran, A. Szytuła, A. Hoser

PII: S0925-8388(16)33979-2

DOI: 10.1016/j.jallcom.2016.12.072

Reference: JALCOM 39994

To appear in: *Journal of Alloys and Compounds*

Received Date: 26 August 2016

Revised Date: 3 December 2016

Accepted Date: 5 December 2016

Collinear antiferromagnetic structure in R_2Ni_2In (R = Er, Tm)

S. Baran[a,*], A. Szytuła[a], A. Hoser[b]

[a] *M. Smoluchowski Institute of Physics, Jagiellonian University, prof. Stanisława Łojasiewicza 11, PL-30 348 Kraków, Poland*
[b] *Helmholtz-Zentrum Berlin für Materialen und Energie GmbH, Hahn-Meitner Pl. 1, D-14 109 Berlin, Germany*

Abstract

R_2Ni_2In (R = Er, Tm) which crystalizes in the orthorhombic structure of the Mn_2AlB_2-type was investigated by powder neutron diffractometry. At low temperatures the rare earth magnetic moments form an antiferromagnetic structure related to the propagation vector $\vec{k} = [\frac{1}{2}, 0, \frac{1}{2}]$. The magnetic moments are parallel to the b-axis and equal to 7.71(7) μ_B and 5.76(4) μ_B for Er and Tm, respectively. In order to verify validity of obtained magnetic structure model a symmetry analysis was performed.

Keywords:
intermetallics, rare earth alloys and compounds, neutron diffraction

1. Introduction

The compounds belonging to the R-Ni-In system (R – rare earth element) take two different crystal structure variants with stoichiometry close to 2:2:1:

- an orthorhombic one of the Mn_2AlB_2-type (space group *Cmmm*), found in the stoichiometric composition R_2Ni_2In (R = Y, Sm, Gd-Tm, Lu) [1, 2],
- a tetragonal one of the Mo_2FeB_2-type (space group $P4/mbm$) found in both stoichiometric composition R_2Ni_2In (R = La, Ce-Nd) and nonstoichiometric one $R_2Ni_{2-x}In$ (x = 0.22, R = Y, Sm, Gd-Tm, Lu) [2].

Studies of physical properties of R_2Ni_2In reveal that Ce_2Ni_2In is a non-magnetic intermediate-valence system [3, 4] while Nd_2Ni_2In orders antiferromagnetically below 8 K [5]. Recent paper on magnetic and thermodynamic properties of R_2Ni_2In (R = Gd-Tm) reports antiferromagnetic ordering in all these compounds [6]. The critical temperatures of magnetic order vary between approximately 5 K (Tm) and 40 K (Tb). In case of R_2Ni_2In (R = Er and Tm), which are reported in this work, the Neél temperature depends slightly on the experimental method used and is equal to 7.2 K (χ_{ac}), 6.5 K (χ_{dc}) or 5.4 K (C_p – heat capacity) for Er_2Ni_2In while for Tm_2Ni_2In is equal to 5.0 K (χ_{ac}), 4.8 K (χ_{dc}) or 4.0 K (C_p). It is worth noting that for Tm_2Ni_2In additional anomalies were observed at 3.3 K (χ_{ac}) and 2.6 K (χ_{dc}). The values of effective magnetic moments suggest that Ni atoms do not carry magnetic moments. Neutron diffraction data indicate existence of antiferromagnetic structure in Tb_2Ni_2In [7]. The structure is related to the propagation vector $\vec{k} = [\frac{1}{2}, 0, \frac{1}{2}]$ and the terbium magnetic moments are parallel to the c-axis.

The nonstoichiometric $R_2Ni_{2-x}In$ (R = Gd-Er) compounds have also been found to order antiferromagnetically with the Néel temperatures ranging from 6.3 K (Er) up to 23.9 K (Tb) [8]. It is worth noting that the Néel temperature of non-stoichiometric compound is smaller than the one of respective stoichiometric compound.

In this work, the magnetic structures of R_2Ni_2In (R = Er, Tm) are reported for the first time. The structures have been derived from neutron powder diffraction data. In addition, a symmetry analysis of allowed magnetic structures is presented.

2. Experimental details

Polycrystalline samples of R_2Ni_2In (R = Er, Tm) were obtained by arc melting of constituent elements (purity 99.9 wt % or better) under argon atmosphere. The obtained ingots were encapsuled in evacuated silica tubes and annealed at 870 K for 1 month. The sample quality was checked by X-Ray powder diffraction at room temperature (PANAlytical X'PERT diffractometer with $Cu_{K\alpha}$-radiation).

Powder neutron diffraction patterns were collected at low temperature (1.5 K or 1.6 K) and at the paramgnetic state (approximately 10 K) on the E6 diffractometer at Helmholtz-Zentrum Berlin für Materialen und Energie GmbH. The incident neutron wavelength was 2.432 Å.

For Rietveld analysis of X-ray and neutron diffractograms the computer program *FullProf* was utilized [9] while for symmetry analysis the computer program *basireps*, which is distributed together with *FullProf*, was used.

3. Crystal structure

The X-ray and neutron diffraction data confirm that the samples crystalize in the orthorhombic crystal structure of the

*Corresponding author. Phone: (+48 12) 6644686; e-mail: stanislaw.baran@uj.edu.pl

Mn_2AlB_2-type (space group *Cmmm*), in agreement with previously published reports [1, 2, 6]. The structure is shown in Fig. 1.

In R_2Ni_2In (R = Er, Tm), the atoms occupy the following Wyckoff sites (centering translation $[\frac{1}{2}, \frac{1}{2}, 0]$ is skipped):

R at $4j$:	$0, y_R, \frac{1}{2}$	$0, 1 - y_R, \frac{1}{2}$
Ni at $4i$:	$0, y_{Ni}, 0$	$0, 1 - y_{Ni}, 0$
In at $2a$:	$0, 0, 0$	

In case of the rare earth atoms, which carry magnetic moments, the local symmetry is *m2m*. While taking into account distances not exceeding 3.5 Å, each rare earth atom is surrounded by non-magnetic elements, namely: 6 Ni atoms and 4 In atoms.

The Er_2Ni_2In sample was found to be single-phased while the Tm_2Ni_2In one contained small amounts of the $TmNi_2$ [10] (5.9 wt %) and $Tm_2Ni_{1.78}In$ [2] (4.8 wt %) impurity phases.

The paramagnetic neutron powder diffractogram of Er_2Ni_2In, taken at 10.1 K, together with its best Rietveld fit is shown in Fig. 2. The refined crystal structure parameters for both Er_2Ni_2In and Tm_2Ni_2In are listed in Table 1.

Table 1: Crystal structure parameters of R_2Ni_2In (R = Er and Tm) as refined from neutron diffraction data collected at 10.1 K (Er) and 10.2 K (Tm) together with corresponding reliability factors.

Compound	Er_2Ni_2In	Tm_2Ni_2In
Crystal structure	Mn_2AlB_2-type	
Space group	*Cmmm*	(No. 65)
a [Å]	3.853(1)	3.852(1)
b [Å]	13.970(3)	13.965(4)
c [Å]	3.606(1)	3.603(1)
V [Å^3]	194.12(6)	193.82(6)
y_R	0.364(1)	0.364(1)
y_{Ni}	0.198(1)	0.197(1)
$R_{profile}$ [%]	2.05	2.39
R_{Bragg} [%]	6.08	6.09
χ^2 [%]	4.72	1.23

4. Magnetic structure

The neutron diffraction patterns, collected at 1.6 K (Er_2Ni_2In) and 1.5 K (Tm_2Ni_2In), show presence of Bragg reflections of magnetic origin which can be indexed with a propagation vector $\vec{k} = [\frac{1}{2}, 0, \frac{1}{2}]$. In order to extract pure magnetic contribution, a set of differential diffraction patterns was calculated by subtracting the paramagnetic data from the patterns taken at lower temperatures. Fig. 3 shows such a differential pattern obtained for Tm_2Ni_2In. The so-derived data were used for the Rietveld-type analysis. The scale factor used while refining magnetic phase was the one found previously for the paramagnetic pattern of the respective compound.

In order to find magnetic structure models allowed by symmetry, a symmetry analysis has been performed. In this approach the magnetic structure is determined by the basis vectors of one irreducible representation of the magnetic group, which is formed by the propagation vector and the space group.

In R_2Ni_2In (R = Er, Tm), the rare earth atoms occupy the $4j$ Wyckoff site with atoms at:

R_{11} at	$0, y_R, \frac{1}{2}$
R_{21} at	$0, 1 - y_R, \frac{1}{2}$

and two remaining ones related to the $[\frac{1}{2}, \frac{1}{2}, 0]$ centering translation:

R_{12} at	$\frac{1}{2}, \frac{1}{2} + y_R, \frac{1}{2}$
R_{22} at	$\frac{1}{2}, \frac{1}{2} - y_R, \frac{1}{2}$

In the case of the *Cmmm* space group, the propagation vector $\vec{k} = [\frac{1}{2}, 0, \frac{1}{2}]$ forms a star together with $\vec{k'} = [-\frac{1}{2}, 0, \frac{1}{2}]$ while all the rare earth atoms at $4j$ site belong to the same orbit. The symmetry analysis gives four one-dimensional irreducible representations $\tau_1, ..., \tau_4$ where τ_1 and τ_3 appear twice while τ_2 and τ_4 appear once (the labeling of representations and basis vectors follows the output of *basireps*). The list of basis vectors is presented in Table 2.

Table 2: Basis vectors of $\tau_1, ..., \tau_4$ as listed for the rare earth atoms R_{11} and R_{21}. The vectors for the remainig R_{12} and R_{22} atoms can be easily calculted by multiplying the below listed vectors by a factor of $\exp(-2\pi i\vec{k} \cdot \vec{\Delta r})$, where $\vec{\Delta r}$ corresponds to the difference in position vectors.

atom	R_{11}	R_{21}
τ_1	$[1, 0, 0]$	$[-1, 0, 0]$
	$[0, 1, 0]$	$[0, 1, 0]$
τ_2	$[0, 0, 1]$	$[0, 0, 1]$
τ_3	$[1, 0, 0]$	$[1, 0, 0]$
	$[0, 1, 0]$	$[0, -1, 0]$
τ_4	$[0, 0, 1]$	$[0, 0, -1]$

The Rietveld refinement of the neutron diffraction patterns, collected at 1.6 K (Er_2Ni_2In) and 1.5 K (Tm_2Ni_2In), unambiguously favors the magnetic structure related to τ_1. The magnetic structure can be writen as $[u, v, 0]$ and $[-u, v, 0]$ for the R_{11} and R_{21} atoms, respectively, where u and v parameters (they can be complex numbers, in general) have to be refined from experimental data. The refinement leads to $u = 0$ and v being a real number. Such a structure can be interpreted as a collinear one with all magnetic moments of the same magnitude being parallel to the b-axis, as shown in Fig. 4. All rare earth magnetic moments are coupled ferromagnetically within one crystallographic unit cell while the adjacent cells are coupled antiferromagnetically along the [100] or [001] directions. The refined parameters of the magnetic structures in R_2Ni_2In (R = Er and Tm) are listed in Table 3. The corresponding magnetic space group is A_bmm2 (#38.193 in the Belov-Neronova-Smirnova notation) or P_Amm2 (#25.8.162 in the Opechowski-Guccione notation). While determining the magnetic space group the symmetry-based computational tools for magnetic crystallography were used [11].

It is worth noting that all Bragg reflections of magnetic origin, present in the differential neutron diffraction pattern of Tm_2Ni_2In (see Fig. 3), are well fitted with the proposed magnetic structure model and no magnetic contribution arising from

Table 3: Magnetic structure parameters of R_2Ni_2In (R = Er and Tm), refined from the neutron diffraction data, collected at 1.6 K (Er_2Ni_2In) and 1.5 K (Tm_2Ni_2In), together with corresponding reliability factors. $\vec{k}$ denotes propagation vector, μ – magnetic moment on R^{+3} while DMM - direction of magnetic moment.

Compound	Er_2Ni_2In	Tm_2Ni_2In
T [K]	1.6	1.5
$\vec{k}$	$[\frac{1}{2}, 0, \frac{1}{2}]$	$[\frac{1}{2}, 0, \frac{1}{2}]$
μ [μ_B]	7.71(7)	5.76(4)
DMM	[010]	[010]
$R_{profile}$ [%]	2.30	2.58
$R_{magnetic}$ [%]	5.64	3.56
χ^2 [%]	6.55	1.29

the impurity phases mentioned in the section *Crystal structure* are detectable.

5. Conclusions and Discussion

Neutron diffraction experiment confirms that the R_2Ni_2In (R = Er and Tm) intermetallics crystalize in the orthorhombic Mn_2AlB_2-type structure (space group *Cmmm*, No. 65) with all rare earth atoms occupying the same $4j$ Wyckoff position. The structure is highly anisotropic – the b-axis is more than four times longer than two remaining ones (see Fig. 1). As a result, a natural multilayer structure is formed. The structure consists of stacked a-c planes containing different elements in sequence In-R-Ni-R-In-R-Ni-R-In. Such a structure should lead to highly anisotropic physical properties.

The low temperature neutron diffraction data confirm antiferromagnetic ordering at low temperatures suggested in the previous report [6]. The positions of Bragg reflections of magnetic origin correspond to the propagation vector $\vec{k} = [\frac{1}{2}, 0, \frac{1}{2}]$. Rietveld refinement together with symmetry analysis led to the magnetic structure model with all rare earth magnetic moments of the same magnitude being parallel to the b-axis. However, in Tb_2Ni_2In the rare earth moments are parallel to the c-axis [7]. In the isostructural R_2Ni_2Pb (R = Dy, Ho, Er) compounds the magnetic moments point at different crystallographic directions depending on the rare earth element considered, namely: they are confined to the a-c plane (Dy) [12], parallel to the c-axis (Ho) [13] or parallel to the b-axis with possible small a-axis component (Er) [14]. Such a result suggest a strong influence of crystalline electric field (CEF). Another evidence of the CEF influence is a reduction of rare earth magnetic moments. The moments found at low temperatures [1.6 K (Er_2Ni_2In) and 1.5 K (Tm_2Ni_2In)] from neutron diffraction data equal 7.71(7) μ_B (Er) and 5.76(4) μ_B (Tm) and are significantly lower than the respective free R^{+3} ion values [9.0 μ_B (Er) and 7.0 μ_B (Tm)]. The reduction of magnetic moments was also observed in the previously reported magnetometric measurements [6].

The results presented in this work suggest no magnetic moment on the Ni atoms. The same conclusion comes from magnetometric measurements [6]. Such a result was also obtained from ab initio calculations for U_2Ni_2X (X = In, Sn) [15, 16].

Acknowledgements

The authors would like to thank Prof. Wiesława Sikora from the AGH University of Science and Technology in Kraków for help in determination of the magnetic space group and Dr Yuriy Tyvanchuk from the Ivan Franko National University of Lviv for the preparation of samples.

This research project has been supported by the European Commission under the 7th Framework Programme through the 'Research Infrastructure' action of the 'Capacities' Programme, NMI3-II Grant number 283883.

[1] V.I. Zaremba, V.A. Bruskov, P.Yu. Zavalii, Ya.M. Kalychak, Inorg. Mater. 24 (1988) 409-411
[2] Ya.M. Kalychak, V.I. Zaremba, V.M. Baranyak, P.Yu. Zavalii, V.A. Bruskov, L.V. Sysa, O.V. Dmytrakh, Inorg. Mater. 26 (1990) 94-96
[3] R. Hauser, H. Michor, E. Bauer, G. Hilscher, D. Kaczorowski, Physica B: Condensed Matter 230âĂŞ232 (1997) 211-213
[4] D. Kaczorowski, P. Rogl, K. Hiebl, Phys. Rev. B 54 (1996) 9891-9902
[5] S. Maskova, S. Danis, A. Llobet, H. Nakotte, L. Havela, Acta Physica Polonica A 126 (2014) 282-283
[6] A. Szytuła, S. Baran, J. Przewoźnik, Yu. Tyvanchuk, Ya. Kalychak, J. Magn. Magn. Mater. 387 (2015) 83âĂŞ89
[7] A. Szytuła, S. Baran, A. Hoser, Ya.M. Kalychak, B. Penc, Yu. Tyvanchuk, Acta Physica Polonica A 124 (2013) 994-997
[8] Yu. Tyvanchuk, S. Baran, T. Jaworska-Gołąb, R. Duraj, Ya.M. Kalychak, A. Szytuła, Acta Physica Polonica A 121 (2012) 678-681
[9] J. Rodriguez-Carvajal, Physica B 192 (1993) 55-69
[10] A. Iandelli, A. Palenzona, in: *Handbook on the Physics and Chemistry of Rare Earths*, edited by K.A. Gschneidner Jr. and L. Eyring, Vol. 2 (1979) ch. 13 pp. 1-54, North-Holland Publishing Company
[11] J.M. Perez-Mato, S.V. Gallego, E.S. Tasci, L. Elcoro, G. de la Flor, M.I. Aroyo, Annu. Rev. Mater. Res. 45 (2015) 217-248
[12] K. Prokeš, E. Muñoz-Sandoval, A.D. Chinchure, J.A. Mydosh, Phys. Rev. B 63 (2003) 134427
[13] K. Prokeš, E. Muñoz-Sandoval, A.D. Chinchure, J.A. Mydosh, Eur. Phys. J. B 43 (2005) 163-174
[14] K. Prokeš, E. Muñoz-Sandoval, A.D. Chinchure, J.A. Mydosh, Phys. Rev. B 78 (2008) 014425
[15] M. Diviš, M. Olšovec, M. Richter, H. Eschrig, J. Magn. Magn. Mater. 140-144 (1995) 1365-1366
[16] S.F. Matar, J. Magn. Magn. Mater. 151 (1995) 263-272

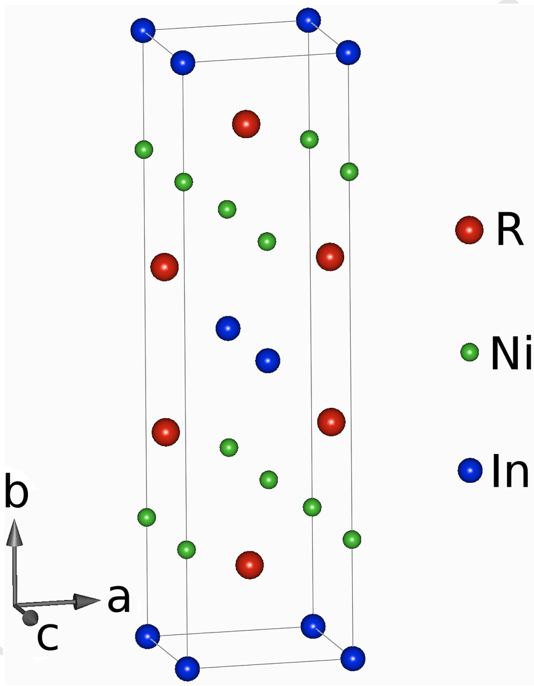
Figure captions

Figure 1: Crystal structure of R_2Ni_2In (R = Er, Tm). It is orthorhombic of the Mn_2AlB_2-type.

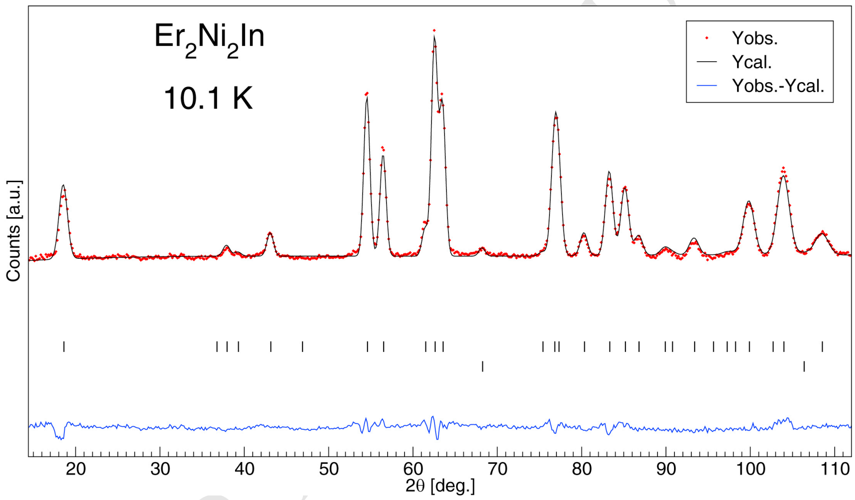
Figure 2: Neutron diffraction pattern of Er_2Ni_2In collected at 10.1 K (paramagnetic state), together with its Rietveld fit and the difference plot. The upper row of vertical ticks indicates positions of Bragg reflections originating from Er_2Ni_2In while the bottom row refers those arising from vanadium sample container.

Figure 3: Differential neutron diffraction pattern of Tm_2Ni_2In constructed as a difference between the experimental data collected at 1.5 K and 10.2 K. The solid line represents the Rietveld fit. The difference plot is shown in the bottom. The vertical ticks indicate positions of Bragg reflections originating from antiferromagnetic structure formed by the rare earth magnetic moments, as decribed in the section *Magnetic structure*.

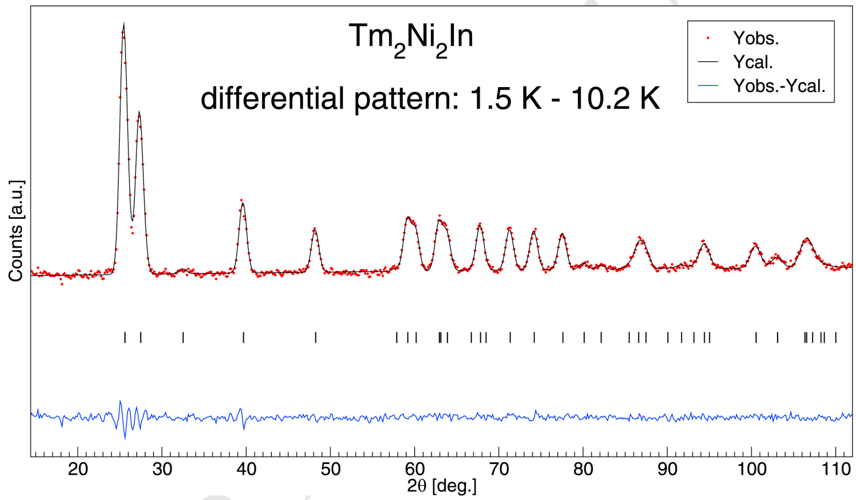
Figure 4: Magnetic unit cell in R_2Ni_2In (R = Er, Tm). It is doubled along the [100] and [001] directions when compared with the crystallographic one.



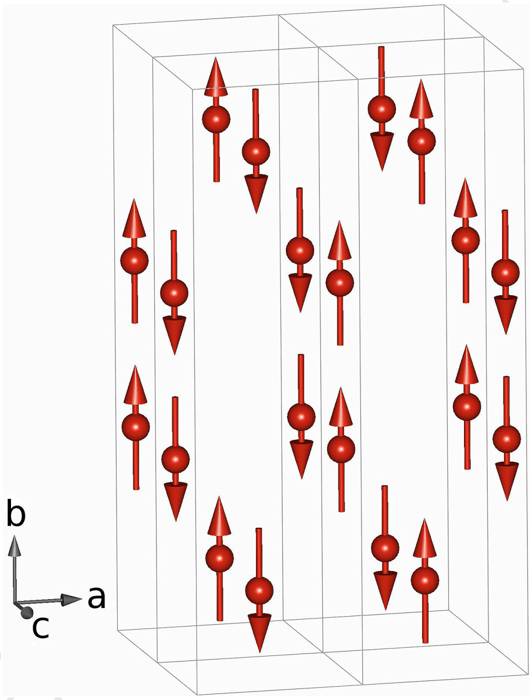
R
Ni
In
b
a
c



Er_2Ni_2In
10.1 K
Yobs.
Ycal.
Yobs.-Ycal.
Counts [a.u.]
2θ [deg.]
20
30
40
50
60
70
80
90
100
110



Tm2Ni2In
differential pattern: 1.5 K - 10.2 K
Yobs.
Ycal.
Yobs.-Ycal.
Counts [a.u.]
2θ [deg.]
20
30
40
50
60
70
80
90
100
110


b
a
c

Highlights

1) magnetic structure in R_2Ni_2In (R = Er, Tm) is reported for the first time
2) the structure is related to the propagation vector k = [1/2,0,1/2]
3) validity of the proposed structure model is verified by symmetry analysis