Incommensurate-commensurate magnetic phase transitions in Tb$_{1-x}$Er$_x$Ni$_5$ compounds

A Pirogov$^{1,2}$, H Lee$^3$, Y N Choi$^3$, E Gerasimov$^{1,2}$, A Lukoyanov$^{1,4}$ and S Bogdanov$^1$

$^1$M.N. Miheev Institute of Metal Physics of the UB of the RAS, S. Kovalevskoy str. 18, 620108 Ekaterinburg, Russia
$^2$Institute of Natural Sciences and Mathematics, Ural Federal University, Kuibysheva 48, 620026 Ekaterinburg, Russia
$^3$Neutron Science Division of Korea Atomic Energy Research Institute, 1045 Daedeok-daero, 305-353 Daejeon, Korea Republic
$^4$Institute of Physics and Technology, Ural Federal University, Mira 19, 620002 Ekaterinburg, Russia

E-mail: pirogov@imp.uran.ru

Abstract. Spontaneous and magnetic field induced incommensurate – commensurate magnetic phase transitions have been studied in Tb$_{1-x}$Er$_x$Ni$_5$ compounds near the critical concentration $x_c = 0.125$. Compounds crystallize in the hexagonal CaCu$_5$ type phase ($P6/mmm$ space group). In compounds with $x \geq x_c$ the magnetic order is a commensurate ferromagnetic one. The samples with $x < x_c$ have an incommensurate structure that is a fan like magnetic structure and described by two propagation vectors. An incommensurate – “lock in” magnetic transition takes place at 10 K at cooling regime.

1. Introduction

Intermetallic compounds of the $R$Ni$_5$ type (where $R$ is a rare earth ion) and their substitution derivatives have been extensively studied in view of a wide variety of physic-chemical properties of these compounds [1-5]. They are applied in hydrogen storage technology owing to their capacity to form hydrides with the high hydrogen concentration. From the physical point of view, the distinctive feature of these compounds is that an energy of magnetocrystalline anisotropy equals and even exceeds an exchange energy. This results in an unusual form of the $x$-$T$ magnetic phase diagram in the $R_{1-x}R_x$Ni$_5$ intermetallics in case of existence of competition between types of magnetic anisotropy of $R$ and $R''$ ions [6]. The $x$-$T$ magnetic diagram represents as two lines that cross at the tetracritical point [7]. In [6, 7] we have investigated Tb$_{1-x}$Er$_x$Ni$_5$ compounds and found that the magnetic structure is an incommensurate for $x = 0$, while it is commensurate and ferromagnetic for $x \geq 0.2$. In TbNi$_5$ we observed the large thermal hysteresis in temperature dependences of Bragg reflections, satellites and the propagation vector $k$ of an incommensurate magnetic structure. Bragg reflections and satellites exhibited opposite intensity dependences in the temperature range (6 – 10) K. Besides, we found that the relatively weak external magnetic field ($H_e = 3.5$ kOe) was enough to suppress an incommensurate ordering in TbNi$_5$. It is worthy to study how an incommensurate structure is transformed to a commensurate structure.
To date several attempts to characterize the magnetic state of TbNi₅ were made by means of first-principles calculations [8]. However, their general weakness is a failure to take into account a spin-orbit coupling.

In this paper we present results of neutron diffraction study of incommensurate – commensurate magnetic phase transitions in Tb₁₋ₓErₓNi₅ compound for x = 0.1 (and additionally x = 0.125) over temperature region (3 – 30) K and under external fields up to 8 kOe.

We also carried out first-principles calculations taking into account spin-orbit coupling and strong electronic correlations in the 4f states of the rare-earth ions.

2. Experimental details
The polycrystalline Tb₁₋ₓErₓNi₅ samples with x = 0.1 and 0.125 have been synthesized by induction melting in alumina crucible under argon atmosphere and homogenized at 1000°C. Metallographic and X-ray analysis testified that both samples were single-phase with the CaCu₅-type structure (Space group P6/mmm).

Neutron powder diffraction (NPD) patterns were recorded with HRPD diffractometer in KAERI. The neutron wavelength was λ = 1.835 Å. Rietveld analysis of the NPD patterns was performed using Fullprof software [9].

The electronic states of TbNi₅ and Tb₀.₉Er₀.₁Ni₅ have been calculated employing the method of the local spin density approximation with Hubbard U-correction for 4f states and spin-orbital coupling [10] within the tight binding, linear muffin-tin orbitals, atomic spheres approximation package.

3. Results and discussion
Figure 1 shows the parts of NPD patterns of the Tb₁₋ₓErₓNi₅ compounds for x = 0, 0.1, and 0.125 at 3 K. The pattern for x = 0.125 displays only Bragg (100), (001), and (101) reflections, containing contributions from nuclear and magnetic scattering. The magnetic structure of this compound is commensurate and the propagation vector k = 0. The Tb-ion magnetic moments are parallel to each other and the basal plane. The R-ion moment is equal to 7.8(1) μB at 3 K.

The patterns for x = 0 and 0.1 show (100), (001), and (101) Bragg reflections as well as (001)⁺, (001)⁻, (101)⁺, and (101)⁻ satellites. Magnetic structures of these compounds are incommensurate and described by two propagation vectors. One of them is the vector k₁ = 0, and another k₂ = 2π/c(0, 0, 0.019) [see 11] and 2π/c(0, 0, 0.027) for x = 0 and 0.1, respectively.

The module of the k₂ vector increases over interval concentrations x = (0 – 0.1) and decreases over interval x = (0.1 – 0.125). So, an incommensurate magnetic phase exists over concentration interval x = (0 – 0.1) and it becomes a commensurate phase at concentration x > 0.125. Thus, incommensurate – commensurate phase transition occurs at the concentration x_cr = 0.125.

Figure 2 presents, as example, NPD patterns for x = 0.1 at 10 K, 20 K, and 30 K on heating regime. Intensities of Bragg reflections and satellites decrease with temperature and a long-range magnetic order is destroyed at T_p = 22 K. Over whole temperature region the best agreement between observed and calculated NPD patterns is achieved just as in the TbNi₅ case [3]: the magnetic structure for x = 0 and 0.1 is described as fan-like structure with two (k₁ and k₂) propagation vectors. The k₁ and k₂ vectors correspond to ferromagnetic and modulated components of the Tb-ion magnetic moment, respectively. A modulated component is the transverse spin wave type. At 3 K the ferromagnetic and modulated components are equal to 3.3(1) μB and 7.4(1) μB, respectively; the total Tb-ion moment is equal to 8.1(2) μB.

Figure 3 displays temperature dependences of the k₂ vector module for x = 0.1 on cooling and heating regimes. As can see from figure 3, the k₂-vector module starts rising at 14 K on heating, while it takes the constant value below 10 K on cooling. Therefore, the k₂ vector exhibits the temperature hysteresis, which is about 4 K.
Figure 1. Parts of observed NPD patterns of a) TbNi$_5$, b) Tb$_{0.9}$Er$_{0.1}$Ni$_5$, and c) Tb$_{0.875}$Er$_{0.125}$Ni$_5$ at 3 K. Data for TbNi$_5$ are from [11].

Figure 2. Observed (points) and calculated (line) NPD patterns of Tb$_{0.9}$Er$_{0.1}$Ni$_5$ obtained on heating regime.

Figure 3. Temperature dependence of the $k_2$-vector module for $x = 0.1$ on heating and cooling regimes.
The temperature, at which the stabilization of the propagation vector appears, is the point of the phase transition between incommensurate and commensurate phases. In Tb$_{0.9}$Er$_{0.1}$Ni$_5$ sample the $k_2$-vector module keeps the constant value at temperatures below 10 K, therefore the sample undergoes the transition from the incommensurate phase to commensurate (lock in) phase.

For $x = 0.1$ temperature evolution of $k_2$ vector is similar to temperature dependence of the $k_2$ in parent TbNi$_5$ compound [11], in which the hysteresis was equaled to about 7 K.

Figure 4 represents, as example, temperature dependences of the (101) satellite for concentrations $x = 0$ and 0.1. It is seen that the satellite intensities show qualitatively different temperature curves for $x = 0$ and 0.1. In TbNi$_5$ the hysteresis of the satellite intensity is distinctly observed. Such the hysteresis also occurs in the case of Bragg reflections. On the contrary, in Tb$_{0.9}$Er$_{0.1}$Ni$_5$ intensities of Bragg reflections and satellites do not show the temperature hysteresis at heating and cooling.

Thus, in the system of Tb$_{1-x}$Er$_x$Ni$_5$ compounds the concentration incommensurate – commensurate phase transition exists at $x_{cr} = 0.125$. Besides, spontaneous incommensurate – “lock in” magnetic phase transformation takes place in compounds with $x = 0$ and 0.1 at low temperatures. This transformation is characterized by a hysteresis in temperature dependences of the propagation vector. In TbNi$_5$ not only the propagation vector, but also Bragg reflections and satellites exhibit large temperature hysteresis. In Tb$_{0.9}$Er$_{0.1}$Ni$_5$ we did not find the hysteresis on temperature dependences of intensities of Bragg reflections and satellites. Since the $k_2$-vector module keeps the constant value below 10 K, therefore, the sample undergoes the “lock-in” – incommensurate phase transition.

The main parameters of crystal and magnetic structures for $x = 0.1$ and 0.125 are given in table 1.

![Figure 4](image-url). Temperature dependences of the (101)–satellite intensity for a) Tb$_{0.9}$Er$_{0.1}$Ni$_5$ and b) TbNi$_5$ [11] in cooling and heating regimes.

![Figure 5](image-url). Field dependence of $k_2$-vector module for $x = 0.1$ at 9 K.
Now we go over a behavior of the Tb$_{0.9}$Er$_{0.1}$Ni$_5$ sample at an external magnetic field. When a magnetic field is applied to this sample, the intensity of satellites decreases and the intensity of Bragg reflections increases. Satellites disappear at the field $H_{cr}$ $\approx$ 2 kOe, while the Bragg reflections grow with field over whole interval (0 – 8) kOe.

Figure 5 shows the field dependence of the $k_2$-vector module at 9 K. It is seen that the module falls almost linearly over interval fields (0 – 1.5) kOe and drops to zero, when the field increases up to 2 kOe. The magnetic structure of the sample is incommensurate and described by two vectors $k_1 = 0$ and $k_2 = 2\pi/c(0, 0, \tau)$ at fields less than $H_{cr}$ and by one vector $k_1 = 0$, if $H \geq 2$ kOe.

Table 1. Main parameters of crystal and magnetic structures of Tb$_{0.9}$Er$_{0.1}$Ni$_5$ and Tb$_{0.875}$Er$_{0.125}$Ni$_5$ at 3 K. The $a$ and $c$ are the lattice constants; Tb/Er, Ni$_{2c}$, and Ni$_{3g}$ are the coordinates of Tb/Er-ions and Ni- atoms at the positions 1$a$, 2$c$ and 3$g$, respectively; $B$ is the temperature factor; $\tau$ is the module of the $k_2$ vector; r.l.u. are the reciprocal lattice units; $\mu_{tot}$ and $\mu_{Ni}$ are the total magnetic moment of Tb/Er ion and Ni atom; $R_{Br}$ and $R_{f}$ are Bragg and profile agreement factors for the crystal structure; $R_{mag}$ is the agreement factor for the magnetic structure.

| Parameter | Dimension | $x = 0.1$ | $x = 0.125$ |
|-----------|-----------|-----------|-----------|
| $a$       | Å         | 4.8821(1)  | 4.8828(1)  |
| $c$       | Å         | 3.9489(1)  | 3.9499(2)  |
| Tb/Er     | $1a$      | (0, 0, 0)  | (0, 0, 0)  |
| $B(Tb/Er)$ | $A^2$    | 0.21(4)    | 0.13(9)    |
| Ni$_{2c}$ | $2c$      | (1/3, 2/3, 0) | (1/3, 2/3, 0) |
| $B(Ni_{2c})$ | $A^2$ | 0.23(3)    | 0.18(6)    |
| Ni$_{3g}$ | $3g$      | (1/2, 0, 1/2) | (1/2, 0, 1/2) |
| $B(Ni_{3g})$ | $A^2$ | 0.23(3)    | 0.18(6)    |
| $\tau$    | r.l.u.    | 0.027      | 0          |
| $\mu_{tot}$ | $\mu_B$ | 8.3(2)     | 7.8(1)     |
| $\mu_{Ni}$ | $\mu_B$ | 0(0)       | 0(0)       |
| $R_{Br}$  | %         | 3.1(1)     | 3.1(1)     |
| $R_{f}$   | %         | 2.2(2)     | 2.2(2)     |
| $R_{mag}$ | %         | 6.1(2)     | 6.1(2)     |

So, the magnetic field induces the transition from the incommensurate magnetic phase to commensurate structure. In the incommensurate phase the ferromagnetic and modulated components of the Tb-ion magnetic moments change drastically in the field range (0 – 1) kOe. The commensurate phase is ferromagnetic. The magnetization is parallel to the basal plane and the total Tb moment is equal to $\mu_{tot} = 8.3(1) \mu_B$ at 8 kOe. This value is lower than the magnetic moment of Tb$^{3+}$ free ion ($9 \mu_B$) and the effective Tb-ion moment (8.7 $\mu_B$), which we obtained in our first principle calculations. It is possible that the low value of $\mu_{tot}$ points to an existence of magnetization fluctuations in the rare-earth subsystem.

We found that an external field had an influence on lattice parameters of the sample with $x = 0.1$. Temperature dependences of $a$ and $c$ lattice constants exhibit a slight jump-wise ($\approx 0.0004$ Å) increasing over the interval (1.5 – 2) kOe. The extension of the lattice at incommensurate – commensurate transition, induced by magnetic field, is agreed with larger lattice parameters for $x = 0.125$ in comparison with that for $x = 0.1$ (see Table 1). This may originate from a spontaneous volume magnetostriction of Tb ions, because the Ni-atom magnetic moment is small to produce an observable effect.

We can make conclusion on the stability of the incommensurate phase upon Er-ion substitution. As mentioned in Introduction, in TbNi$_5$ the incommensurate phase is suppressed at magnetic field $H_{cr} = 3.5$ kOe. In the case of Tb$_{0.9}$Er$_{0.1}$Ni$_5$, the incommensurate phase is suppressed at smaller
magnetic field $H_{\text{cr}} = 2$ kOe. Hence, we can conclude that a stability of incommensurate structure decreases with increasing the concentration $x$ in Tb$_{1-x}$Er$_x$Ni$_5$.

A change of the magnetic state of Tb$_{0.9}$Er$_{0.1}$Ni$_5$ can be observed studying the intensity of the background on the NPD patterns with an external field. Such the field dependence shows that the intensity of the background decreases abruptly at $H \approx 0.5$ kOe. This indicates that a partially disordered magnetic state transforms into a relatively ordered state, which exists over the interval $(1 - 5)$ kOe. The further lowering of the background indicates a suppression of magnetization fluctuations by an external field.

Now we present results of first principles calculations. The electron structure of TbNi$_5$ and alloys doped with copper TbNi$_5$Cu$_x$ was calculated in local spin density approximation (LSDA) [12] without the spin-orbital coupling though this coupling is one of essential interactions in rare-earth metals. Besides, the 4f states of the Tb ions were not treated, they were taken as a part of the core. In this reason the 4f states were absent in density of states picture. Moreover, it was proposed in [12] that Tb-ion magnetic moments rotate along the $a$ - axis producing Tb moment component to the $c$ - axis. This assumption disagrees with all experimental results about TbNi$_5$.

In our LDA+U+SO [13] first principles calculations for TbNi$_5$ and Tb$_{0.9}$Er$_{0.1}$Ni$_5$ we have given proper weight the 4f states into the orbital basis for strong electron correlations as well as the spin-orbital coupling. This allowed obtaining both spin and orbital moments to proper calculate the total and effective Tb-ion moments. In this first principles method, we obtained that the Tb moments lie on the basal plane. The spin moments of the Er ions are directed along the $c$-axis. As a result of this, in the calculated densities of states for $x = 0$ and 0.1, the structure of the 4f state peaks represents the splitting due to the spin-orbit coupling and crystal field together. It is worth to note these effects are absent in previous calculations.

The calculated values of spin and orbital moments of the Tb ion are equal to $S_{\text{Tb}} = 2.8$ and $L_{\text{Tb}} = 3.0$, respectively. The total moment $J_{\text{Tb}} = 5.8$ and the effective Tb moment $g_{\text{Tb}}J_{\text{Tb}} = 8.7$ $\mu_B$ for Lande factor $g_{\text{Tb}} = 3/2$. This magnetic moment value is close to the one obtained in the neutron diffraction experiment. Regarding the Ni - atom moment we found that it has a negligible spin moment module (about $0.01$ $\mu_B$).

The Tb$_{0.9}$Er$_{0.1}$Ni$_5$ electron configuration calculations result in $S_{\text{Er}} = 1.4$ and $L_{\text{Er}} = 6.0$, which give the total moment of $J_{\text{Er}} = 7.4$ and the effective magnetic moment $g_{\text{Er}}J_{\text{Er}} = 8.9$ $\mu_B$ for $g_{\text{Er}} = 6/5$. The Ni spin moment was equal to 0.03 $\mu_B$.

The calculated exchange parameter for pairs of the 4f ions revealed the presence of competing ferro- and antiferromagnetic interactions with the nearest and next nearest Tb – Tb neighbors. This competition causes an incommensurate magnetic structure.

4. Conclusion

The neutron diffraction study of the hexagonal Tb$_{0.9}$Er$_{0.1}$Ni$_5$ and Tb$_{0.875}$Er$_{0.125}$Ni$_5$ intermetallic compounds has been performed.

The Tb$_{0.9}$Er$_{0.1}$Ni$_5$ compound possesses the incommensurate fan like structure, which is described by two ($k_1 = 0$ and $k_2 = 2\pi c(0, 0, \tau)$) propagation vectors and two (ferromagnetic and modulated) components of the Tb-ion magnetic moment. The modulated component develops as a transverse spin wave. The sample changes to a paramagnetic state at $T_p = 22$ K.

The magnetic structure of Tb$_{0.875}$Er$_{0.125}$Ni$_5$ is commensurate and ferromagnetic. The incommensurate – commensurate magnetic phase transition occurs at concentration $x_{\text{cr}} = 0.125$ at 3 K.

The sample with $x = 0.1$ undergoes the incommensurate – “lock in” magnetic transition at $T_f = 10$ K in cooling regime and at 14 K in heating. The temperature dependence of the $k_2$-vector magnitude shows hysteresis of about 4 K.

The external magnetic field $H_{\text{cr}} = 2$ kOe induces the incommensurate – commensurate phase transition in Tb$_{0.9}$Er$_{0.1}$Ni$_5$.

The electron structures of the TbNi$_5$ and Tb$_{0.875}$Er$_{0.125}$Ni$_5$ compounds were calculated accounting for both strong electron correlations in the 4f shell and spin-orbital coupling. In accordance with
calculations one can assume that competing ferro- and antiferromagnetic interactions with the nearest and next nearest Tb – Tb neighbours cause an incommensurate magnetic structure.

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References
[1] Senoh H, Takechi N, Takeshita H T, Tanaka H, Kiyobayashi T and Kuriyama N 2004 Mat. Sci. and Engin. B 108 96
[2] De Oliveira N A 2017 J. Phys. and Chem. of Sol. 103 13
[3] von Ranke P J, Mota M A, Grangeice D F, Magnus A, Carvalho G, Caldas A, De Oliveira N A and Gama S, 2004 Phys. Rev. B 70 134428
[4] Radwanski R J, Michalski R, Ropka Z and Blaut A 2002 Physica B 319 78
[5] Haldar A, Dhiman I, Das A, Suresh K G and Nigam A K 2011 J. All. Comp. 509 3760
[6] Lee S, Park J-G, Podlesnyak A A, Prokeš K, Sikolenko E V, Ermolenko A S, Gerasimov E G, Dorofeev Yu A and Vokhmyanin A P 2005 JETP Lett. 82 34
[7] Pirogov A N, Park J-G, Ermolenko A S, Korolev A V, Kuchin A G, Lee Seongsu, Choi Y N, Park Junghwan, Ranot Mahipal, Yi Junghwan, Gerasimov E G, Dorofeev Yu A, Vokhmyanin A P, Podlesnyak A A and Swainson I P 2009 Phys. Rev. B 79 174412
[8] Monir Mohammed El Amine, Baltach Hady, Monchaal Younes and Murtaza G 2018 J. Supercond. and Novel Magn. 31 547
[9] Rodriguez-Carvajal J 1993 Phys. B 192 55
[10] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 J. Phys.: Cond. Mat. 9 767
[11] Lee S, Pirogov A N, Park J-G, Swainson I P, Dorofeev Yu A, Teplykh A E, Ermolenko A S, Gerasimov E G and Podlesnyak A.A 2003 Europhys. Lett. 62 350
[12] Lizarraga R, Bergman A, Björkman T, Liu H-P, Andersson Y, Gustafsson T, Ermolenko A S, Kuchin A G, Nordström L and Eriksson O 2006 Phys. Rev. B 75 094419
[13] Shorikov A O, Lukoyanov A V, Korotin M A and Anisimov V I 2005 Phys. Rev. B 72 024458