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# Effect of Tb/Gd Substitution on Crystal Structure and Exchange Interactions of $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$ Intermetallic Compounds

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In the paper an influence of Tb/Gd substitution on crystal structure and exchange interactions of  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  ( $x = 0.0, 0.5, 0.8, 1.0$ ) polycrystalline compounds have been studied. The crystal structure of all samples was checked at the room temperature by means of X-ray diffraction. Exchange integrals of R–R ( $J_{\text{RR}}$ ), T–T ( $J_{\text{TT}}$ ) and R–T ( $J_{\text{RT}}$ ) atoms were evaluated from  $M(T)$  magnetization curves (2–300 K, 2 T) based on the mean field theory calculation. As it was shown the samples examined are single phase and crystallize in the  $\text{PuNi}_3$  (space group  $R-3m$ ) type of crystal structure. The Tb/Gd substitution causes the decrease of lattice parameters as well as the volume of the unit cell. With increase of the  $x$  parameter the magnetic moment of Tb atoms increases from  $6.94 \mu_{\text{B}}$  ( $x = 0.5$ ) to  $8.12 \mu_{\text{B}}$  ( $x = 1$ ). The  $M(T)$  dependence of the examined compounds depends almost 8 times stronger on exchange interactions within the R–R site than the interactions between the two antiferromagnetically coupled magnetic sublattices R–T.

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## 1. Introduction

Intermetallic compounds of rare earth (R) and transition (T) elements are very interesting from scientific point of view because of a mixture of localized (R) and itinerant (T) magnetism [1–6]. Generally, in a crystal structure magnetic properties of the transition elements are susceptible to their surroundings regarding the fact that responsible for magnetism  $3d$  electronic band partially overlaps conduction band. In contrast to this the rare-earth (R) elements such as gadolinium and terbium have a localized magnetic moment of  $4f$  electrons (internal shell) which are shielded by outer electronic shells. Magnetic interactions between  $4f$  (R) and  $3d$  (T) electrons are possible only via conduction electrons of R elements which leads to an appearance of the two antiferromagnetically coupled R and T sublattices. Gadolinium as an element with orbital momentum  $L = 0$  (no spin-orbit coupling) is usually non-sensitive for crystal field and therefore in intermetallic compounds retains its magnetic moment of  $7 \mu_{\text{B}}$ . In the case of terbium ( $L > 0$ ) the strong spin-orbit coupling makes its magnetic moment dependent on the crystal structure. Therefore, partial substitution of Tb by Gd atoms in R–T type of intermetallic compounds causes not only a change of their average magnetic moment but also can influence internal exchange interactions. The aim of the paper is to study crystal structure and exchange interactions (based on the MFT calculations) of  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  ( $x = 0, 0.5, 0.8, 1$ ) intermetallic compounds.

## 2. Experimental details

The polycrystalline samples  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  ( $x = 0.0, 0.5, 0.8, 1.0$ ) were prepared by arc-melting from high purity elements (Gd — 99.9%, Tb — 99.9%, Ni — 99.99%) under argon atmosphere. To ensure homogeneity the samples were remelted several times. Afterwards all samples were wrapped in tantalum foil, placed in quartz tubes and annealed at  $900^\circ\text{C}$  for one week. The crystal structure of all samples was checked by means of X-ray diffraction (XRD) using Siemens D5000 diffractometer. XRD measurements were done at the room temperature. Magnetization  $M$  of the examined samples was measured with the use of SQUID magnetometer (MPMS XL7 Quantum Design) in the temperature range of 2–300 K and magnetic field equals 2 T.

## 3. Results and discussion

The analysis of the diffraction patterns shows that the  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  samples are single phase and in the whole range of studied concentrations crystallize in the  $\text{PuNi}_3$  (space group  $R-3m$ ) type of crystal structure. In this structure the rare earth atoms are located in two inequivalent positions:  $\text{R}_I$  3a (0, 0, 0) and  $\text{R}_{II}$  6c (0, 0,  $z$ ) where  $z = 0.1414$ . The transition metals elements occupy three positions with different structure environment:  $\text{T}_I$  3b (0, 0,  $1/2$ ),  $\text{T}_{II}$  6c (0, 0,  $z$ ) where  $z = 1/3$  and  $\text{T}_{III}$  18h ( $1/2, -1/2, z$ ) where  $z = 0.0829$ . In the present studies the Rietveld method has been applied to refine the crystal structure. In this method the FullProf program was used.

The X-ray diffraction line profile has been done by using pseudo-Voigt function. Besides crystal structure pa-

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parameters also background coefficients, temperature coefficients, occupation numbers and full width of half maximum (FWHM) have been refined. The Rietveld analysis showed that the values of occupation numbers for each position are similar. The change of the lattice parameters obtained from the refinement show that Tb/Gd substitution causes the decrease of all unit cell parameters (see Fig. 1). It is obvious because terbium atoms have smaller ionic radius (1.00 Å) than gadolinium atoms (1.02 Å). Moreover the values of  $a$  and  $c$  parameters for  $\text{GdNi}_3$  and  $\text{TbNi}_3$  compounds are close to previously obtained [1, 4, 7]. The refinement of occupation indicates that Tb atoms prefer to occupy 6c position. The occupation number of this position in all doped compounds is almost twice higher than 3a site.

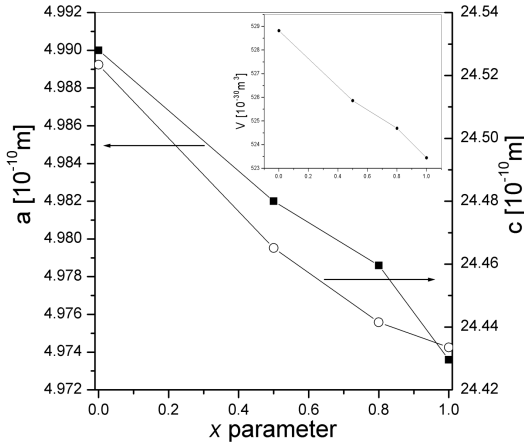


Fig. 1. Lattice parameters and volume of the unit cell (inset) for the  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  compounds.

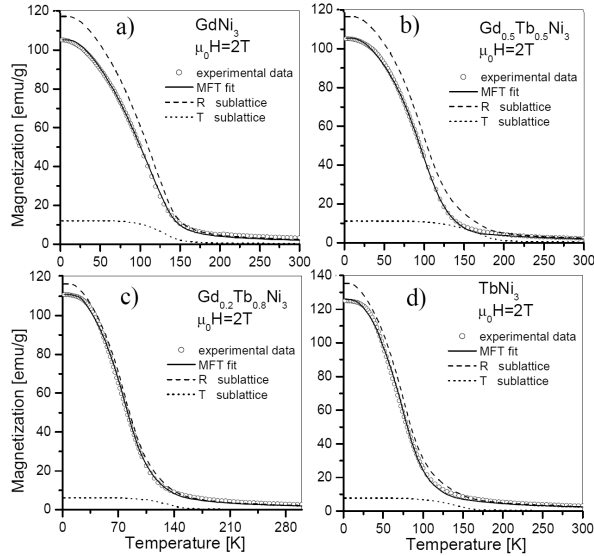


Fig. 2. Thermomagnetic curves  $M(T)$  and MFT analysis for the  $\text{Gd}_{1-x}\text{Tb}_x\text{Ni}_3$  ( $x = 0.0, 0.5, 0.8, 1.0$ ) compounds.

Figure 2 shows  $M(T)$  thermomagnetic curves, for all studied compounds, and result of the following MFT analysis. With the assumption that magnetic moments of R and Ni atoms are coupled antiferromagnetically, one can determine magnetization of the system  $M$  as a superposition of the two R (site R) and Ni (site T) sublattices, i.e.,  $M = |M_R - M_T|$ . In the MFT approximation one can describe magnetization of the sites [8–10]:

$$\begin{aligned} M_R &= -N_R \mu_B g_R \langle J_R \rangle \\ &= -N_R \mu_B g_R J_R B \left( \frac{g_R J_R H_R}{k_B T} \mu_B \right), \\ M_T &= -N_T \mu_B g_T \langle J_T \rangle \\ &= -N_T \mu_B g_T J_T B \left( \frac{g_T J_T H_T}{k_B T} \mu_B \right), \end{aligned} \quad (1)$$

$$\begin{aligned} H_R &= \frac{2J_{RR}Z_{RR}(g_R - 1)^2}{N_R g_R^2 \mu_B^2} M_R \\ &+ \frac{2J_{RT}Z_{RT}(g_R - 1)(g_T - 1)}{N_T g_R g_T \mu_B^2} M_T + H_{\text{EXT}} \\ H_T &= \frac{2J_{TR}Z_{TR}(g_R - 1)(g_T - 1)}{N_R g_R g_T \mu_B^2} M_R \\ &+ \frac{2J_{TT}Z_{TT}(g_T - 1)^2}{N_T g_T^2 \mu_B^2} M_T + H_{\text{EXT}}, \end{aligned} \quad (2)$$

where  $B$  is the Brillouin function,  $N$  is a number on corresponding atoms per unit volume,  $\mu_B$  is the Bohr magneton,  $g$  is the Landé factor,  $J$  is total angular momentum,  $H$  is magnetic field acting on the corresponding site,  $H_{\text{EXT}}$  is an external field,  $k_B$  is the Boltzmann constant. Making use Eqs. (1) and (2) one can determine the exchange integrals of R–R ( $J_{RR}$ ), T–T ( $J_{TT}$ ) and R–T ( $J_{RT} = J_{TR}$ ) sites via fitting the dependences to the empirical thermomagnetic curves. The fact that the Brillouin function possesses different curvature for different ground state allows determining also  $J_R$  and  $J_T$  if the parameters are considered as independent. In the case of Tb one can expect that atoms take different positions with different magnetic moments. The presented analysis refers to an average value of magnetic moment on this site. The external magnetic field of 2 T was chosen in order to saturate the samples and what follows avoid an influence of magnetic domain structure on  $M(T)$  dependence. From the XRD analysis one can determine average coordination numbers of R–R, R–T, T–R and T–T surroundings that equal 6, 12, 4.5, 8 respectively. In the case of  $x = 0.5$  and  $x = 0.8$  it was assumed that the R site consists of two kinds of rare-earth atoms (described by the Brillouin functions with different ground states) with one average exchange integral within the site. Additionally, assuming that magnetic moment of Gd atoms is  $7 \mu_B$ , one can calculate magnetic moment of Tb and Ni atoms (in the ground state).

TABLE

The Curie temperature  $T_C$ , exchange integrals, magnetic moment of Tb atoms  $\mu_{\text{Tb}}$  and Ni atoms  $\mu_{\text{Ni}}$  for all the studied compounds.

Compound	$T_C$ [K]	$J_{\text{RR}}$	$-J_{\text{RT}}$	$J_{\text{TT}}$	$\mu_{\text{Tb}}$	$\mu_{\text{Ni}}$
		[ $10^{-23}$ J]			[ $10^{-21}$ J]	[ $\mu_B$ ]
GdNi <sub>3</sub>	114	1.58	7.05	2.01	–	0.24
Gd <sub>0.5</sub> Tb <sub>0.5</sub> Ni <sub>3</sub>	100	2.05	1.85	3.54	6.94	0.22
Gd <sub>0.2</sub> Tb <sub>0.8</sub> Ni <sub>3</sub>	72	1.62	1.63	4.12	7.46	0.11
TbNi <sub>3</sub>	65	1.18	1.42	4.41	8.12	0.16

The best fitting quality was obtained with the parameters listed in Table where the Curie temperatures determined as inflection points of the  $M(T)$  curves are additionally included. Let us notice that with increase of Tb content the Curie temperature decreases from 114 K to 65 K for the GdNi<sub>3</sub> and TbNi<sub>3</sub>, respectively. Simultaneously, with increase of the  $x$  parameter the magnetic moment of Tb atoms increases and antiparallel aligned magnetic moment of Ni atoms decreases. Let us discuss the obtained values of exchange integrals  $J_{\text{RR}}$ ,  $J_{\text{TT}}$  and  $J_{\text{RT}}$ . Taking into account that the  $\mu_{\text{Ni}}$  values are relatively low,  $J_{\text{TT}}$  parameter does not significantly influence the MFT fit quality and only  $J_{\text{RR}}$  and  $J_{\text{RT}}$  are responsible for the change of the  $M(T)$  dependence. The Curie temperature reflects exchange interaction so according to the MFT theory a relation of  $T_C \sim J$  is expected to be present. In our case the  $J_{\text{RR}}$  values reveal a maximum at  $x = 0.5$  and the  $J_{\text{RT}}$  parameter decreases with a decrease of  $T_C$  but the main change of  $J_{\text{RT}}$  is observed between the compounds with  $x = 0$  and  $x = 0.5$ . It seems that in our case  $T_C$  can be proportional to a combination of  $J_{\text{RR}}$  and  $J_{\text{RT}}$ . A balance between these two quantities can be found by a definition of, let us say, an apparent exchange integral  $J_{\text{AP}} = aJ_{\text{RR}} + |J_{\text{RT}}|$  and searching a proper value of  $a$  for which  $T_C \sim J_{\text{AP}}$ .

Figure 3 presents such linear correlation and the best result was obtained for  $a = 7.76$ . The slope does not have a physical meaning but the value of  $a$  indicates how many times  $J_{\text{RR}}$  influences the  $M(T)$  dependence stronger than  $J_{\text{RT}}$ .

#### 4. Conclusions

The main conclusions of the paper can be summarized as follows:

i) All studied samples crystallize in the PuNi<sub>3</sub> crystal structure. The Tb/Gd substitution causes the decrease of lattice parameters as well as the volume of the unit cell. The refinement of the crystal structure indicates that terbium atoms prefer localization in the 6c position more than 3a.

ii) In the presented MFT approximation model one can state that with the increase of the  $x$  parameter the magnetic moment of Tb atoms increases from 6.94  $\mu_B$

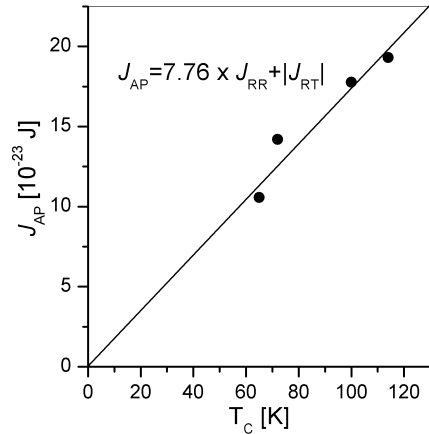


Fig. 3. Correlation between apparent exchange integral  $J_{\text{AP}} = 7.76J_{\text{RR}} + |J_{\text{RT}}|$  and the Curie temperature  $T_C$ .

( $x = 0.5$ ) to 8.12  $\mu_B$  ( $x = 1$ ). The  $J_{\text{RR}}$  values reveal a maximum at  $x = 0.5$ . The  $J_{\text{RT}}$  parameter decreases with a decrease of  $T_C$  and the main change of  $J_{\text{RT}}$  is observed between the compounds with  $x = 0$  and  $x = 0.5$ . The  $M(T)$  dependence of the examined compounds depends almost 8 times stronger on exchange interactions within the R–R site than the interactions between the two antiferromagnetically coupled magnetic sublattices R–T.

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