Magnetic properties of the TbNi$_2$Mn$_x$ ($0 \leq x \leq 1$) cubic structure compounds

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Abstract. The structure and magnetic properties of TbNi$_2$Mn$_x$ compounds have been studied by the X-ray and neutron powder diffraction, magnetization and magnetostriction measurements. It was found that the compounds for $x < 1$ crystallize in a cubic MgCu$_2$ Laves phase structure, in spite of the R to 3d-metal ratio changes from 1:2 to 1:3. TbNi$_2$Mn shows a superstructural ordering ($F\bar{4}3m$ space group). Magnetic measurements revealed a substantial growth of the Curie temperature from 29 K for TbNi$_2$ up to a maximum value of 160 K for TbNi$_2$Mn$_{0.5}$. Monotonous decrease of the magnetization, magnetostriction and increase of the coercivity are observed with the Mn alloying. The obtained data are interpreted assuming the formation of a magnetic moment at Ni site and a non-collinear arrangement of the Tb-ion magnetic moments.

1. Introduction

Intermetallic compounds of rare earth (R) and 3d-transition (T) metals with the cubic MgCu$_2$-type Laves phase structure were the subject of extensive studies in the past decades owing to their relatively simple structure and outstanding magnetic properties, such as giant magnetostriction [1] and a large magnetocaloric effect [2]. The formation of the Laves phase is limited by the ratio of the atomic radii of the constituents (from 1.10 to 1.30) and the concentration of valence electrons per atom [3]. No homogeneity range is usually observed for the binary RT$_2$ compounds.

Recently, Wang et al. [4] have found that the RNi$_2$Mn alloys with R = Tb, Dy, Ho and Er crystallize in the MgCu$_2$-type structure. Their Curie temperatures ($T_C$) were found to be considerably higher than the $T_C$ values of the corresponding RNi$_2$ and RMn$_2$ compounds. The largest value $T_C=131$ K was reported for TbNi$_2$Mn. The spontaneous magnetic moment of TbNi$_2$Mn determined from the bulk magnetization measurements amounts to 4.8 $\mu_B$ per formula unit (f.u.) [4], which is considerably smaller than the value of $g_J\mu_B = 9 \mu_B$ for free Tb$^{3+}$ ion. Assuming that the Ni atoms give a negligible contribution to the magnetic moment of RNi$_2$Mn, Wang et al. suggest that the Mn atoms have a rather large magnetic moment directed oppositely to the moment of the Tb atoms.

Since both TbNi$_2$ and TbNi$_2$Mn$_x$ are reported to have similar structure, one can assume the existence of a solid solution for some range of the Mn contents. In this paper, we present the results of X-ray and neutron diffraction, magnetization and magnetostriction study of TbNi$_2$Mn$_x$ compounds for different $x$. 
2. Experimental details

The TbNi$_2$Mn$_x$ compounds for $x = 0, 0.25, 0.5, 0.75, 1, 1.25$ and $1.5$ were prepared by induction melting of the pure elements in alumina crucible. An excess of Mn (5 wt.%) was added to compensate the Mn evaporation during the melting and subsequent annealing. The samples were annealed at 870°C for one week.

X-ray powder diffraction measurements have been performed on a DRON-type diffractometer with Cr Kα radiation. Neutron powder diffraction data were collected on the D-3 diffractometer with the neutron wavelength $\lambda = 2.424$ Å at IMP, Zarechny. Magnetization curves were measured using an induction technique in pulsed magnetic fields up to 15 T with the pulse duration time 8 ms in the temperature range 4.2 - 200 K. Magnetostriction was measured by strain gages using the dc current bridge in steady fields produced by an electromagnet.

3. Results and discussion

The fragments of X-ray diffraction patterns of TbNi$_2$Mn$_x$ compounds for different $x \leq 1$ are presented in Fig.1. It is seen that all the samples have the cubic bcc structure as the main phase. The compositions with higher Mn content are found to contain a considerable amount of Tb$_6$(Ni,Mn)$_{23}$ phase. The diffraction pattern of TbNi$_2$Mn shows a few relatively weak reflections, such as (200) and (420), which are forbidden for the C15-type structure. These data imply that the structure of the TbNi$_2$Mn alloy corresponds to a subgroup of the Fd3m space group.

Since the neutron scattering lengths of Tb, Ni and Mn atoms are substantially different, the (200) and (420) reflections are clearly seen in neutron diffraction experiments (Fig. 2). The best fitting of the room-temperature neutron diffraction pattern for paramagnetic TbNi$_2$Mn was achieved within the $F\bar{4}3m$ space group [5]. The atomic positions and site-occupancy factors are listed in Table 1. According to these data, the chemical formula of the compound can be

![Figure 1. Room-temperature X-ray diffraction patterns of TbNi$_2$Mn$_x$ compounds for different $x$.](image1)

![Figure 2. Neutron diffraction patterns of TbNi$_2$Mn compound at 295 K (a) and 4.2 K (b). Symbols represent experimental data, lines - calculated with the parameters listed in Table 1.](image2)
Table 1. Results of the refinement of neutron diffraction patterns for the atomic positions, site occupancies and magnetic moments in the \(\text{F}3m\) space group of the TbNi\(_2\)Mn compound \((a = 7.1842 \text{ Å}, R_{Br} = 2.2\%, R_f = 1.6\%, \chi^2 = 3.3\) for \(T = 295\) K; \(\chi^2 = 12.8, R_{Br} = 3.5\%, R_f = 2.5\%, \) and \(R_{mag} = 5.3\%\) for \(T = 4.2\) K.)

| Atom | Site | \(x/a\) | \(y/a\) | \(z/a\) | Occupancy coefficient at 295 K | Average moment per site \((\mu_B)\) | Moment per atom \((\mu_B)\) |
|------|------|---------|---------|---------|-----------------------------|-----------------------------|-----------------------------|
| Tb   | 4a   | 0       | 0       | 0       | 0.538(1)                    | 4.2(2)                      | 9                           |
| Mn   | 4a   | 0.25    | 0       | 0       | 0.462(1)                    | -1.37(20)                   | -1.37(20)                   |
| Tb   | 4c   | 0.25    | 0.25    | 0.25    | 1.0                         | 5.4(2)                      | 5.4(2)                      |
| Mn   | 16e  | 0.624(1)| 0.624(1)| 0.624(1)| 0.196(1)                    | -0.49(3)                    | -1.37(20)                   |
| Ni   | 16e  | 0.624(1)| 0.624(1)| 0.624(1)| 0.804(1)                    | -0.3(2)                     | -0.3(2)                     |

rewritten as \((\text{Tb}_4)^{4c}(\text{Tb}_{2.15}\text{Mn}_{1.85})^{14a}(\text{Ni}_{12.86}\text{Mn}_{3.14})^{16e}\) which corresponds to the composition \(\text{TbNi}_{2.09}\text{Mn}_{0.81}\). Our attempts to fix the composition \(\text{TbNi}_2\text{Mn}\) and/or to introduce vacancies lead to an increase in the agreement factors.

Since both the low- and high-temperature neutron diagrams contain the same reflections (Figs. 2a and b), the wave vector of a magnetic structure is \(\mathbf{k} = 0\). We performed a symmetric analysis of magnetic structures which could be realized in the TbNi\(_2\)Mn compound (the details are given in [5]). It was found that the moments of the ions occupying the 4a- and 4c-sites are parallel to each other, but they are antiparallel to the moments at the 16e positions. Refining the magnetic structure of TbNi\(_2\)Mn we fixed the atomic positions and site occupancies as they were at room temperature. The refined values of the average moments at the 4a-, 4c- and 16e-positions are listed in Table 1. The total magnetic moment is 5.0(7) \(\mu_B/\text{f.u.}\), which is in agreement with the previous bulk magnetization measurements, 4.8 \(\mu_B/\text{f.u.}\) [4] and 5.59 \(\mu_B/\text{f.u.}\) [6]. In order to determine the values of the Tb-, Mn-, and Ni-ion moments from the average moments at the 4a, 4c, and 16e sites we assume that the moments of Mn atoms at the 4a- and 16e-positions are the same and the Tb moment at the 4a position cannot exceed its free-ion value 9 \(\mu_B\). In these assumptions we obtained the Tb-, Mn-, and Ni-ion moments, which are presented in last column of Table 1. It is seen that, on contrary to binary RNi\(_2\) compounds, Ni ions possess magnetic moment \(\sim 0.3 \mu_B\) in TbNi\(_2\)Mn.

The formation of R-Ni compounds is accompanied by the 3d-5d hybridization and the charge transfer of the 5d electrons to the 3d band. As a result, the 3d-band moment collapses, and Ni ions possess only a small induced moment in RNi\(_2\) compounds. Since Mn has less 3d-electrons than Ni, alloying with Mn may cause electron transfer from the Ni to the Mn 3d-subband, which may lead to splitting the Ni subband. On the other hand, the appearance of the Ni magnetic moment will lead to an increase in both T-T and R-T exchange interactions, which corroborate well with the observed growth of the Curie temperature.

We measured magnetization curves for TbNi\(_2\)Mnx compounds with different Mn content for various temperatures. Using the Arrott plots we determined the temperature of magnetic ordering and the spontaneous magnetization at 4.2 K. As seen form Fig. 3, the Curie temperature is small for TbNi\(_2\). It increases with increasing Mn content, reaches its maximum value 160 K for Mn concentration \(x\) between 0.5 and 0.75 and then gradually decreases. The spontaneous magnetization gradually decreases with Mn alloying. The value of the spontaneous moment 4.7 \(\mu_B/\text{f.u.}\) for TbNi\(_2\)Mn is in good agreement with the data of neutron diffraction. Therefore, the reasons of the magnetization decrease in TbNi\(_2\)Mnx system with increasing \(x\) is the appearance of magnetic moments of Mn and Ni oriented opposite to the Tb moment.
The Tb-containing Laves phase compounds have a high cubic magnetic anisotropy at low temperatures [7]. We found that TbNi$_2$ has a low coercivity at 4.2 K, but the coercivity substantially increases with Mn alloying (Fig. 4). Since a considerable increase in the anisotropy can hardly be expected, the coercivity growth reflects the formation of a magnetically non-uniform state. The partial magnetic disordering is evidenced also by a presence of broad maxima of the magnetic diffusive scattering near the (111) and (220) reflexes in Fig. 2b.

TbNi$_2$ compound has a giant magnetostriction at low temperature [8]. Therefore, it is of interest to study the effect of Mn alloying on the anisotropic magnetostriction $\lambda_\parallel - \lambda_\perp$. As seen from Fig. 4, $\lambda_\parallel - \lambda_\perp$ drastically decreases with increasing Mn content. Since the magnetostriction is an even effect, such behavior can be explained by formation of local areas with the uniaxial anisotropy. Considering the reduced value of Tb-ion moment at the 4c site for TbNi$_2$Mn (Table 1) we conclude that these local areas have different mutual orientations of the Tb moments. The formation of the non-collinear magnetic structure may be due to different local environments of the Tb ions caused by Mn substitution of Tb and Ni sites in the parent cubic Laves phase.

Acknowledgments

The study is supported by Russian Foundation for Basic Research (grant No 07-02-00219), contract No 02.518.11.7119 and the Program of Presidium of RAS Nos 5 and 24.

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