Study of Condensed Matter by Neutron Scattering and Complementary Methods

Neutron Diffraction Studies of $Tb_2Ni_{2-x}In$ Intermetallic Compounds

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The magnetic ordering of the Tb $_2Ni_{1.78}In$ and Tb_2Ni_2In have been studied by neutron diffraction measurements. $Tb_2Ni_{1.78}In$ with the tetragonal Mo $_2FeB_2$-type (space group $P4/mbm$, $tP10$) is antiferromagnet with the Néel temperature equal to 20 K. Below this temperature Tb moments form collinear magnetic structure commensurate with the crystal, described by the propagation vectors equal to (1/4, 1/4, 1/2). Magnetic moment equal to 7.60(6) μ_B is parallel to c-axis. The Tb_2Ni_2In in the orthorhombic Mn $_2$ lB_2-type (space group $Cmmm$, $oC10$) was detected as an impurity in the studied sample. It orders antiferromagnetically below $\approx$ 100 K with collinear moment arrangement described by the propagation vector (1/2, 1/2, 1/2). t 1.6 K $\mu_{Tb} = 6.33(14)$ μ_B and is parallel to the c-axis.

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1. Introduction

Magnetic materials are of particular interest and importance in both fundamental and applied research [1]. Interesting group of intermetallic compounds may be found in the R–Ni–In (R = rare earth elements) system. According to Ref. [2], rare earth elements form 22 ternary compounds of the R_2Ni_2In and $R_2Ni_{2-x}In$ ($x = 0.22$) type.

The X-ray diffraction data indicate that investigated in this work $Tb_2Ni_{1.78}In$ and Tb_2Ni_2In compounds crystallize in the following structure types:

- $Tb_2Ni_{1.78}In$ in the tetragonal structure of Mo_2FeB_2-type (space group $P4/mbm$, $tP10$, $Z = 2$) [3], which is a ternary derivative of the binary U_3Si_2-type [4],
- stoichiometric composition Tb_2Ni_2In has the orthorhombic structure of the Mn_2 lB_2-type (space group $Cmmm$, $oC10$, $Z = 2$), related to the Mo_2FeB_2-type [5].

The details concerning these structures are discussed in the second part of the work.

The magnetic properties have been determined only for some Tb–Ni–In compounds. Temperature dependence of the magnetic susceptibility and magnetization indicate the ferromagnetic behavior with T_c equal to 70 K in TbNiIn [6] and antiferromagnetic with T_N equal to 20.2 K in $Tb_2Ni_{1.78}In$ compounds [7]. Temperature dependence of magnetic susceptibility of Ce_2Ni_2In (Mo_2FeB_2-type) indicate the intermediate valence behavior [8, 9], while magnetic and specific heat measurements carried out for Nd_2Ni_2In (Mo_2FeB_2-type) indicate antiferromagnetic order below $T_N = 8$K [10].

In this paper we report the results of the X-ray and neutron diffraction measurements as the function of temperature for $Tb_2Ni_{1.78}In$ and Tb_2Ni_2In compounds. From these data the crystal and magnetic structure parameters of these compounds versus temperature are determined.

2. Experimental details

The sample of the total weight of 3.5 g was obtained by the standard melting procedure of high-purity raw metals (Tb-3N, Ni-4N and In-5N): the appropriate for the nominal compositions amounts of the elements were arc-melted under pure argon on a water cooled copper crucible with a tungsten electrode and titanium serving as a getter. To ensure good homogeneity, the sample was annealed at 870 K for 1 month.

The X-ray powder diffraction pattern was recorded at room temperature using a STOE ST DI P diffractometer, with Cu $K_{\alpha 1}$ radiation, curved Ge (111) monochromator transmission geometry, measured interval $6 \leq 2\theta \leq 100°$ in scan step mode, step size in $2\theta = 0.015°$.

The FullProf program [11] package was used for X-ray phase and the Rietveld analysis of the collected data set.

Neutron diffraction data were collected with the E6 powder diffractometer located at the Helmholtz-Zentrum Berlin. The specimen with mass of about 3 g was encapsulated in a cylindrical vanadium container. Neutron diffraction patterns were collected between 1.5 and 100 K with the incident neutron wavelength of 2.440 . Refine-

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ments of the neutron data were made using the FullProf program [11].

3. Results

3.1. Crystal structure

The X-ray at room temperature and neutron diffraction data at 100 K of the synthesized sample indicate that the strong intensity peaks correspond to the tetragonal structure Mo_2FeB_2 (space group $P4/mbm$), while the small intensity peaks are connected with the orthorhombic phase of the Mn_2 lB_2 structure type (space group $Cmmm$).

In the tetragonal structure the Tb atoms occupy 4 h site: $(x, 1/2+x, 1/2)$, Ni atoms 4 g site: $(x, 1/2+x, 0)$ and In atoms 2a site: (0, 0, 0).

In the orthorhombic structure Tb atoms are in 4j site $(0, y, 1/2)$, Ni atoms in 4i site: $(0, y, 0)$ and In atoms in 2a site: (0, 0, 0).

TABLE

Crystal structure parameters of Tb $_2$Ni$_{1.78}$In and Tb_2Ni_2In together with residuals for profile and integrated intensities. The parameters were derived from paramagnetic neutron diffraction patterns collected at 100 K.

Compounds	$Tb_2Ni_{1.78}In$	Tb_2Ni_2In
a [ ]	7.3558(8)	3.9046(16)
b [ ]	7.3558(8)	14.1276(67)
c [ ]	3.6565(4)	3.6800(12)
V [^{3}]	197.845(65)	203.00(24)
Tb	4h (x) 0.1789(5)	4j (y) 0.3703(14)
Ni	4g (x) 0.3799(4)	4i (y) 0.2007(10)
In	2a	2a
R_{Bragg} [%]	9.0	13.4
R_{F} [%]	6.7	11.7

The refinement of the paramagnetic neutron diffraction pattern taken at 100 K has yielded crystallographic parameters of both phases. The results are listed in Table and define the part of individual phases: 90 wt% tetragonal and 10 wt% orthorhombic. The determined parameters are in good agreement with the previous X-ray data [3, 5].

3.2. Magnetic structure

The neutron diffraction pattern collected at 30 K (see Fig. 1b) contains additional Bragg reflections originating from magnetic order. They should come from the orthorhombic phase, because the magnetic data for tetragonal phase give the Néel temperature equal to 20.2 K [4]. These reflections can be indexed with the use of the propagation vector $\boldsymbol{k} = (1/2, 1/2, 1/2)$. Similar propagation vector is determined for the magnetic order in the isostructural Er_2Ni_2Pb compound [12]. In the crystallographic unit cell of Tb_2Ni_2In compound the Tb atoms are in following positions: Tb1 $(0, y, 1/2)$, Tb2 $(0, \bar{y}, 1/2)$,

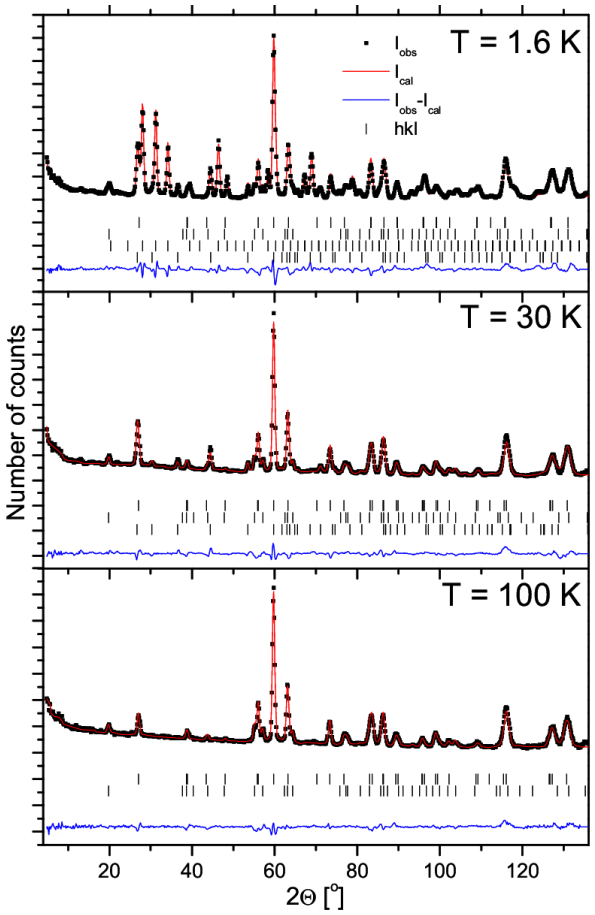

Fig. 1. Neutron diffraction patterns of Tb $_2$Ni$_{2-x}$In measured at different temperatures equal to (a) 100 K, (b) 30 K, and (c) 1.5 K. In all patterns the squares represent experimental points. The solid lines are: the calculated profile for crystal and magnetic structure models (as is described in the text) and difference between the observed and calculated intensities (at the bottom of each diagram). The vertical bars indicate the positions of nuclear (first top and third rows) and magnetic (second fourthly row) for Tb $_2$Ni$_{1.78}$In and Tb_2Ni_2In, respectively.

Tb3 $(1/2, 1/2+y, 1/2)$ and Tb4 $(1/2, 1/2-y, 1/2)$. The irreducible representation gives six models of the magnetic order (see Table II in Ref. [12]). The best agreement with the experimental one is obtained for the model in which Tb moments equal to 2.31(4) μ_{B} are parallel to the c-axis with the sequence of the signs $++-+$ in crystallographic unit cell ($R_{\mathrm{mag}} = 16.9\%$).

On the neutron diffraction pattern collected at 1.5 K (see Fig. 1c) besides the peaks observed at 30 K the additional peaks are present. ll these reflections can be indexed with the use of the propagation vector $\boldsymbol{k} = (1/4, 1/4, 1/2)$. Terbium magnetic moments occupy in $Tb_2Ni_{1.78}In$ compound the 4h positions with moments at Tb1 $(x, 1/2+x, 1/2)$, Tb2 $(\bar{x}, 1/2-x, 1/2)$, Tb3 $(1/2+x, \bar{x}, 1/2)$ and Tb4 $(1/2-x, x, 1/2)$. The best agreement with experimental data are obtained for the

following sequence of the signs $++--$ for Tb moments in the crystallographic unit cell. Tb moments equal to 7.60(6) μ_B is parallel to the c-axis ($R_{mag} = 8.1\%$). In orthorhombic phase Tb moments equal to 6.33(14) μ_B and parallel to the c-axis form similar magnetic order like that in 30 K ($R_{mag} = 10.6\%$).

Temperature dependence of the values of the magnetic moments in $Tb_2Ni_{1.78}In$ compound (see Fig. 2) gives the Néel temperature equal to 21 K for the tetragonal phase, in good agreement with the results obtained from the magnetic data. The Néel temperature for the orthorhombic phase determined by magnetic measurements is equal to ≈ 100 K [13].

The lattice parameter a and the unit cell volume V determined for tetragonal phase increase with increasing temperature, while the c lattice parameter decreases (see Fig. 2). This indicates the existence of the magnetoelastic effect.

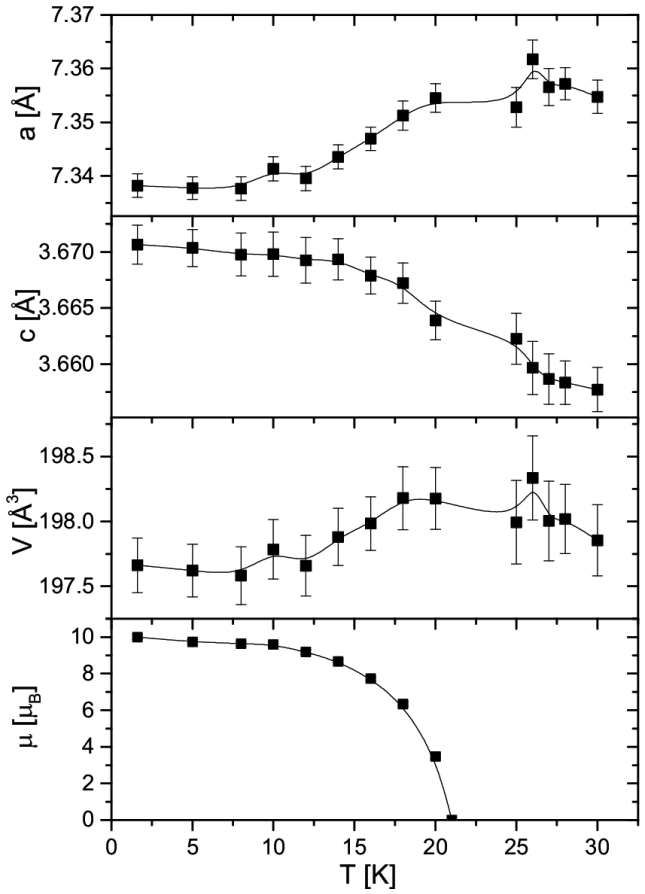

Fig. 2. Temperature dependence of the values of the lattice parameters a and c, unit cell volume V and the Tb magnetic moments for $Tb_2Ni_{1.78}In$ compound.

4. Discussion

The results presented in the work give the parameters of the crystal and magnetic structures of two compounds — $Tb_2Ni_{1.78}In$ and Tb_2Ni_2In. Determined in 100 K parameters of the crystal structure are in good agreement with those determined from X-ray data at room temperature. The analysis of the positions and intensities of the Bragg reflections indicate that the crystal structures are stable up to 1.5 K. Comparison of the both crystal structures is shown in Fig. 3. The Tb_2Ni_2In and $Tb_2Ni_{1.78}In$ structures are two-dimensional in direction of the shortest cell parameter, i.e. layers of terbium atoms alternate with layers of Ni and In. In the Tb_2Ni_2In structure Ni atoms form zigzag chains along the x-axis (Ni–Ni distances 2.394 Å), whereas in $Tb_2Ni_{1.78}In$ only separate pairs Ni–Ni (Ni–Ni distances 2.499 Å) are observed. The shortest Tb–Tb distances are 3.673 Å in Tb_2Ni_2In and 3.657 Å $Tb_2Ni_{1.78}In$, respectively to data in Table.

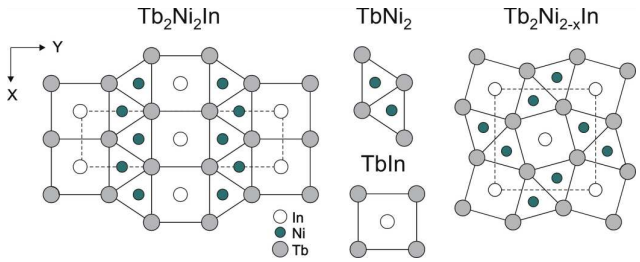

Fig. 3. Comparison of the Tb_2Ni_2In and $Tb_2Ni_{1.78}In$ crystal structures: left — the projection on the (001) plane in Tb_2Ni_2In; right — projection on the (001) plane for $Tb_2Ni_{1.78}In$.

Accordingly to [14, 15], structures of Tb_2Ni_2In (Mn_2lB_2-type) and $Tb_2Ni_{1.78}In$ (Mo_2FeB_2-type) represent homologous series $R_{m+n}M_{2n}X_m$ where m and n are the numbers of CsCl (TbIn) and lB_2 ($TbNi_2$) related slabs, respectively. For the both structures $m = n = 2$.

Both compounds are antiferromagnets with the Néel temperature equal to 21 K for $Tb_2Ni_{1.78}In$ and ≈ 100 K for Tb_2Ni_2In, respectively. The Tb moments form collinear antiferromagnetic structure described by the propagation vectors equal to (1/4, 1/4, 1/2) for first and (1/2, 1/2, 1/2) for the second. The direction of the magnetic moments is different: in $Tb_2Ni_{1.78}In$ magnetic moment is parallel to the c-axis as well perpendicular to the layer (a–a), while in Tb_2Ni_2In the moment is parallel to the short c-axis. The values of the Tb magnetic moment are smaller than that for free Tb^{3+} ion value equal to 9.0 μ_B, which indicates influence of the crystal electric field.

The magnetic structure of $Tb_2Ni_{1.78}In$ is different from these observed in isostructural $U_2T_2X_2$, where T is d-electron element and X = Sn, In. In all these compounds magnetic ordering is described by the propagation vector $\boldsymbol{k}$ = (0, 0, 0) or (0, 0, 1/2). The moments in (001) plane form collinear or non collinear ordering (see Figs. 6 and 7 in Ref. [16]).

In Ce_2Pd_2Sn in intermediate region the modulated magnetic structure with the propagation vector equal to $\boldsymbol{k} = (k_x, 0, 0)$ is observed. With decrease of the temperature the change to the collinear one described by the $\boldsymbol{k} = (0, 0, 0)$ is observed [17].

A modulated ordering of the praseodymium and neodymium magnetic moment with propagation vector $\boldsymbol{k} = [0, 0, 1/2]$ and $[1/4, 1/4, 0]$ below the Néel temperatures $T_N = 5$K and 8 K is evident for Pr_2Pd_2In and Nd_2Pd_2In, respectively [18].

In R_2Ni_2Pb (R = Dy, Ho) compounds the magnetic order is observed with the two commensurate propagation vectors $\boldsymbol{k}_1 = (0, 0, 0)$ and $\boldsymbol{k}_2 = (1/3\ , 0, 0)$ for R = Dy [19] and one $\boldsymbol{k} = (1/5, 0, 0)$ for R = Ho [20].

In Er_2Ni_2Pb the complex magnetic order is observed. With the increase of the temperature the change of the type of magnetic structure is observed [12].

For both compounds $Tb_2Ni_{1.78}In$ and Tb_2Ni_2In the Tb–Tb interatomic distances are large. This indicates that the interaction between Tb moments is of the Ruderman–Kittel–Kasuya–Yosida (RKKY) type. In this case the Néel temperature is expected to be a function of the de Gennes factor $(g_J - 1)^2 J(J + 1)$ where g_J is the Landé splitting factor and J is the total angular momentum of the corresponding magnetic ion. For $R_2Ni_{2-x}In$ compounds this relation is not fulfilled (see Fig. 4 in Ref. [7]) which indicates the influence of the crystal electric field (CEF). Competition of two interactions: RKKY and CEF lead to complicated magnetic structures [21].

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