submitted to J.Phys.: Conference Series

The change of anisotropy in TbNi(Al,In) compounds studied by low temperature x-ray diffraction

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Abstract. We have investigated the transition between the easy-axis and easy-plane type of magnetocrystalline anisotropy in the TbNi(Al,In) series. These compounds crystallize in the hexagonal ZrNiAl-type structure and order magnetically at low temperatures. TbNiAl is an antiferromagnet below 47 K with the moments aligned along the c-axis, whereas TbNiIn orders magnetically below 70 K with moments perpendicular to the c-axis. The presented study is based mainly on the low temperature x-ray powder diffraction performed in presence of external magnetic field. We have revealed that the transition between both types of anisotropy occurs in compounds with In concentration around 30%.

1. Introduction
The ternary RTX compounds (R = rare earth, T = transition d-metal, X = p-metal) crystallizing in the hexagonal ZrNiAl-type structure (space group P62m; see figure 1) form a large group of compounds showing interesting magnetic properties. The type of magnetic order is very sensitive to the number of conduction electrons. On the other hand, the magnetocrystalline anisotropy seems to strongly influence the ratio of lattice parameters. This feature is most noticeable in the Tb-based compounds showing the strongest anisotropy. The substitution of Al by In in the TbNiAl1−xInx series is isoelectronic, but involves a large change of lattice parameters. Therefore, the changes of magnetic properties are primarily driven by this structural change.

TbNiAl orders antiferromagnetically below \( T_N = 47 \) K with a propagation vector of \((1/2 \ 0 \ 1/2)\) [1, 2]. The Tb magnetic moments are aligned along the hexagonal c-axis, but one third of moments remains reduced to almost zero due to a geometrical frustration. The frustrated moments start to propagate along different equivalent direction, e.g. with propagation vector \((-1/2 \ 1/2 \ 1/2)\), below further magnetic phase transition at \( T_1 = 23 \) K and finally all the Tb moments reach the same value at \( 2 \) K. The metamagnetic transition to a ferromagnetic state occurs when applying external magnetic field of \( \approx 0.4 \) T along the c-axis, whereas the magnetic structure is almost insensitive to magnetic fields applied perpendicular to the c-axis [2]. TbNiIn orders magnetically around \( T_{ord} = 70 \) K and the AC-susceptibility indicated additional magnetic phase transitions at \( T_1 = 59 \) K and \( T_2 = 29 \) K [3]. As inferred from neutron diffraction, the Tb moments lie within the basal plane and form a non-collinear structure with \((0 \ 0 \ 0)\) propagation below \( T_{ord} \) and additional weaker component develops below \( T_2 \) [4, 5].
2. **Experimental**

Polycrystalline $\text{TbNiAl}_\infty \text{In}_x$ samples were prepared by arc-melting of pure elements ($3N$ for Tb, $4N5$ for Ni, $5N5$ for Al and $6N$ for In) in a mono-arc furnace under the protection of an argon atmosphere. A higher evaporation of In (approximately two or three orders of magnitude) was considered before weighing individual elements. The X-ray diffraction patterns obtained using Cu $K_\alpha$ radiation showed single-phase samples with the ZrNiAl-type structure.

The low-temperature X-ray diffraction measurements were performed on a Bragg-Brentano diffractometer (Siemens D-500) equipped with helium gas flow cryostat (Oxford Instruments CF1108T) on powder samples fixed by acetone on the Si plate. The diffraction patterns were recorded for $2\theta$ range of 20 - 140 degrees with the step of 0.05 degree by using position-sensitive detector (Braun). Filtered radiation of the cobalt tube (Co $K_\alpha$) was employed. The temperature of the samples was stabilized within 0.1 K by the ITC-503 temperature controller operating with the RhFe resistor. The diffraction patterns were taken for various temperatures: all samples at 300, 100 and 20 K, selected samples also at 200 and 5 K. Measurements were performed first at the room temperature in zero magnetic field. Consequently, permanent magnet made of sintered Sm$_2$(Co, Fe, Cu, Zr)$_{17}$ alloy (Vacomax 225HR, Vakuumschmelze) was placed under the sample holder. It produced a magnetic field of approximately 1 T perpendicular to the sample surface. The room-temperature pattern was then taken again and revealed identical results as the zero-field measurement. The temperature was then gradually lowered to the selected temperatures and the diffraction patterns were taken always at stabilized temperature. The refinement of the structure parameters from the diffraction patterns was done using the Rietveld analysis employing the Fullprof program [6].

3. **Results and discussion**

Diffraction pattern of pure TbNiAl measured at 20 K (i.e. below $T_N$ in the presence of the magnetic field reveals a strongly textured powder (see figures 2 and 3). Observed increase in intensity of the $(0 0 l)$ reflections indicated macroscopic ordering of crystallites with the c-axis parallel to the direction of the external magnetic field. This is in agreement with the results of neutron diffraction and magnetization showing ferromagnetic order with moments aligned along the c-axis in 1 T [2]. Diffraction patterns of In poor compounds ($x < 0.3$) show similar behavior as pure TbNiAl, but the increase of intensity on the $(0 0 l)$ peaks becomes less prominent. We can observe also the strongest peaks other than $(0 0 l)$ (see figure 4). The intensity of $(001)$ and $(002)$ reflections are still clearly enhanced in the sample with $30\%$ of In, but the preferred orientation is much weaker compared to TbNiAl (see figures 3 and 4). Very small difference
between the 300 and 20 K patterns is observed for 40% of In and the texture seems to disappear completely for \( x > 0.4 \) as can be seen from figure 4. This is in agreement with the complex non-collinear magnetic structure reported for TbNiIn [4, 5].

**Figure 2.** The textured powder on TbNiAl\(_{0.9}\)In\(_{0.1}\) sample after measurement and heating to the room temperature.

**Figure 3.** X-ray diffraction patterns at temperatures above and below magnetic phase transition. Strongest peaks are described by indices \((h\ k\ l)\).
Figure 4. X-ray diffraction patterns at temperatures above and below magnetic phase transition. Strongest peaks are described by indices $(h \ k \ l)$. 
The concentration dependence of lattice parameters is approximately linear as can be seen from table 1 and figure 5. The lattice parameter $a$ increases with increasing the In content, whereas the parameter $c$ decreases. This observation can be well understood as the Al(In) atoms lie only within one of the two layers (see figure 1) and the replacement of Al by larger In causes expansion in this layer. The large difference between pure TbNiAl and $x = 0$ sample is due to the fact that TbNiAl undergoes structural change (change of the lattice parameters only, not the crystallographic structure itself) around 100 K [7]. Our study revealed that no such change occurs for the rest of the series as can be seen from figure 5 for the $x = 0.1$ compound. This change, in fact, could not be expected here because the $c/a$ ratio is far from the critical region [7].

The temperature development of the lattice parameters reflects also the change of the magnetocrystalline anisotropy. When comparing the data above and below the temperature of magnetic ordering (300 and 20 K, respectively), the $c/a$ ratio increases for compounds with $x$ up to 0.2 and stays nearly unchanged for the rest of the series (see table 1 and figure 5). This is probably related to the change of magnetocrystalline anisotropy around $x = 0.3$ as indicated by the observed change of the preferred orientation in magnetic field. More detailed temperature dependence of the lattice parameters should be performed to make an unambiguous statement about the relation between structural and magnetic parameters (see reference [8] for comparison).
Table 1. Lattice parameters of TbNiAl$_{1-x}$In$_x$ at temperature above and below the magnetic phase transition.

| x   | a (pm)  | c (pm)  | c/a  | a (pm)  | c (pm)  | c/a  |
|-----|---------|---------|------|---------|---------|------|
| 0.0 | 700.5(3)| 388.5(2)| 0.5545(3)| 696(24)| 398(17)| 0.572(23)|
| 0.1 | 706.0(9)| 386.4(5)| 0.5472(8)| 701(6)| 388(4)| 0.553(6)|
| 0.2 | 713(1) | 385.6(6)| 0.541(1)| 710(1)| 386(1)| 0.544(1)|
| 0.3 | 717(1) | 384.1(6)| 0.535(1)| 715(4)| 384(2)| 0.537(3)|
| 0.4 | 721(2) | 383.6(7)| 0.532(1)| 719(3)| 383(2)| 0.533(3)|
| 0.5 | 725(2) | 382.0(8)| 0.527(2)| 724(2)| 381(1)| 0.526(1)|
| 0.6 | 730(2) | 381(1) | 0.522(2)| 729(2)| 380(1)| 0.522(2)|
| 0.7 | 733(3) | 380(1) | 0.518(2)| 733(3)| 379(1)| 0.517(2)|
| 0.8 | 736(3) | 378(1) | 0.514(2)| 735(3)| 378(1)| 0.514(2)|
| 0.9 | 737(3) | 377(1) | 0.512(2)| 737(3)| 376(1)| 0.510(2)|
| 1.0 | 739(3) | 377(1) | 0.510(2)| 739(3)| 376(2)| 0.508(2)|

4. Conclusions
The X-ray diffraction patterns of the TbNiAl$_{1-x}$In$_x$ series collected in presence of magnetic field below the respective magnetic ordering temperatures clearly indicated transition from the uniaxial anisotropy of TbniAl to a more complex non-collinear magnetic structures of the In rich compounds. The anisotropy change occurs for compounds with In concentration around 30%.

Acknowledgments
The work was supported by the Grant Agency of the Czech Republic under the Grant no. 202/08/0711, the work of M. K. was also supported by the grant SVV-2010-261303. This work is a part of the research program MSM 0021620834 financed by the Ministry of Education of the Czech Republic.

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