Pressure effect on the isostructural transition in RNiAl compounds (R=Tb and Gd)

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Abstract. We have studied the presence of a gap of forbidden $c/a$ values for the hexagonal crystal structure of TbNiAl and GdNiAl, appearing in the whole family of the RTAl compounds (R-rare earth, T-transition metal). TbNiAl and GdNiAl both exhibit a first-order structural transition at low temperatures around 100 K and 205 K, respectively. We have for the first time studied this structural step upon application of hydrostatic pressure on both compounds. An unusually rapid decrease of the critical temperature with pressure was found. The decrease is furthermore steeper for GdNiAl in which the transition appears at higher temperature at ambient pressure. Common property for both studied compounds is preference of the $c/a$ ratio below the critical forbidden interval after application of pressure, due to weaker interplanar chemical bonding in the layered ZrNiAl-type of crystal structure.

1. Motivation

TbNiAl and GdNiAl belong to a large group of compounds crystallizing in the hexagonal ZrNiAl-type of structure. Within recent years, physics of the discontinuity in the temperature or composition dependence of the lattice parameters ($a$ and $c$) observed in several compounds of this family of intermetallics has been of particular interest among others because of influencing other physical properties and namely causing significant troubles when measuring bulk properties like specific heat or electrical resistivity [1-4]. These materials have in common a specific “forbidden” value of the $c/a$ ratio. This conclusion has been corroborated by ab initio calculations [1].

Both studied compounds show very interesting physical properties which have been intensively studied by various experimental techniques [1,2,5-12]. They crystallize in the hexagonal ZrNiAl-type structure and are the most appropriate stoichiometric compounds showing the abrupt transition in the temperature development of the lattice parameters at around 100 K or 205 K, respectively [1,13]. This structural transition, which is generally observed in compounds with the ZrNiAl-type structure, resides in a sudden change of the lattice parameters when the $c/a$ ratio approaches the critical region between 0.565 and 0.575 in the temperature or composition dependence [1]. The crystal structure with the $c/a$ ratio from this forbidden region is energetically less favorable and these $c/a$ values are usually not realized. During the transition, the $a$ and/or $c$ parameters change by several percent to jump over the forbidden $c/a$ region [1] while the evolution of the unit-cell volume is not affected by the transition. Application of hydrostatic pressure - a powerful tool to influence directly interatomic distances in the matter - brings a new dimension into this problem. The pressure influence on structural properties of TbNiAl and GdNiAl is a subject of this paper.
Although the dramatic structure change is hardly observable in the temperature dependence of the specific heat, it is accompanied with a clear change of the effective magnetic moment, change of the crystal field energy spectra and namely with increasing amount of mechanical defects in the sample. We use the advantage of reflecting the increased number of defects in the lattice on the resistivity data, which allow us to follow the structural transition with pressure by using our in-house equipment.

2. Experimental

TbNiAl and GdNiAl polycrystalline samples were prepared by arc melting in the monoarc furnace under protection of Ar atmosphere. The samples were turned and remelted several times to ensure better homogeneity. The lattice parameters and the phase purity of the samples were verified by the X-ray powder diffraction and the composition was confirmed by the electron microscope with EDX analyzer.

We used a double layered (outer CuBe bronze + inner NiCrAl alloy) clamped pressure cell for generation of hydrostatic pressure. A Daphne oil 7373 [14,15] was used as the exchange pressure medium and the thermally stabilized manganin wire was used to determine the pressure inside the pressure cell at room temperature. For cooling we used the two stage closed-cycle refrigerator (Janis Research) and a lock-in amplifier (SRS 830) for acquiring the data of resistivity.

3. Results and discussion

The crystal structure of TbNiAl at room temperature is classified as the hexagonal ZrNiAl-type structure with the low c/a ratio of lattice parameters. By cooling, the structural transition to the high c/a structural phase occurs at \( T_{st}\approx 100 \text{ K} \) as clearly demonstrated by X-ray diffraction [1]. Due to fairly high relative change of the parameters \( a (\sim 0.7\%) \) and \( c (\sim 1.5\%) \), the number of defects in the lattice is increasing and thus the structural transition is generally accompanied by a sudden step in the resistivity measurements with higher resistivity in the high c/a (= above the forbidden c/a range) phase as found for several Gd-based compounds (see e.g. [2,3]). Our not-only-single experience from measurements of the temperature dependence of resistivity can be represented by the figure 1, which shows a broken sample after passing through the transition point at ambient pressure. When applying pressure, the sample is kept together by the external pressure which allows us to continue with the measurement down to lower temperatures and higher pressures.

![Figure 1](image)

**Figure 1.** A photographic view of one of the studied samples after trial to measure the temperature dependence of resistivity. The sample broke after passing the critical temperature \( T_{st} \) at which the step-like change of the lattice results in deteriorating quality of the crystal.

We followed the sudden step in the resistance as an indication of the structural transition while applying the hydrostatic pressure. At ambient pressure, we observe clear steps related to the structural transition at approximately \( T_{st}^{an} \approx 120 \text{ K} \) and \( T_{st}^{up} \approx 135 \text{ K} \) in the cooling and heating mode, respectively, for TbNiAl, and \( T_{st} \approx 205 \text{ K} \) for GdNiAl. In the case of GdNiAl we could follow only the cooling curve. After passing through the critical temperature, the sample was broken. The temperature of the structural transition remains almost unchanged under low pressures up to 0.25 GPa for TbNiAl, then decreases with increasing pressure and finally no phase transition is observed for pressures \( \geq 0.55 \text{ GPa} \). The deduced p-T structural phase diagram is plotted in figure 2. In the lower part of this figure we plot the diagram of GdNiAl based on similar process of the structural transition
determination. The difference in the GdNiAl case is much more rapid decrease of the critical temperature with pressure, what is also reason for much lower number of measured pressure points. Although the exact values of transition temperatures might depend on the sample quality (see also [1]) and pressure history, the main trend is clear: the application of hydrostatic pressure stabilizes the low c/a phase. This result is well in agreement with the observed pressure dependence of the lattice parameters measured at the room temperature [16]. The linear compressibility along the c-axis is more than twice higher than the compressibility along the a-axis [16]. The c/a ratio consequently decreases with increasing pressure, moving away from the forbidden c/a region.

4. Conclusions
The structural transition which lies in the step-like change of the c/a ratio in TbNiAl and/or GdNiAl was followed by resistivity measurements. It occurs around 100 K and 205 K in ambient pressure for TbNiAl and GdNiAl, respectively, and shifts to lower temperatures in applied hydrostatic pressure. The transition vanishes above 0.55 GPa and 0.31 GPa, respectively. The application of hydrostatic pressure thus stabilizes the low c/a phase in both cases what is natural consequence of weaker interplanar bonding between the layers in the hexagonal ZrNiAl-type structure.

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