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EFFECTS OF HYDROGEN ABSORPTION IN TbNiAl AND UNiAl.

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Hydrides (deuterides) of TbNiAl and UNiAl have been widely studied because of drastic increase of magnetic ordering temperature under hydrogenation. Here we report neutron-diffraction results of the three deuterides, TbNiAlD_{1.28}, TbNiAlD_{0.8} and UNiAlD_{2.23}

Although hydrides of intermetallic compounds are used extensively as hydrogen-storage media¹, little is known about the exact nature of metal-hydrogen interactions. However, this knowledge is of essential importance for the understanding of thermodynamic and other properties.

The antiferromagnetics TbNiAl and UNiAl are known to crystallize in the hexagonal ZrNiAl type structure (space group P-62m)^{2,3}. Magnetic order in intermetallic TbNiAl is based on well-defined 4f moments, which are coupled by indirect exchange interaction of RKKY type. Ehlers and Maletta⁴ found that this compound undergoes two magnetic phase transitions around 23 and 47 K, forming complex magnetic structure. They reported, based on neutron-diffraction data, that magnetic ordering occurs in two Tb sublattices, described by two different propagation vectors, i.e. $\mathbf{q} = (1/2, 1/2, 1/2)$ and $\mathbf{q} = (1/2, 0, 1/2)$. Recently, it was shown that introduction of hydrogen (deuterium) into TbNiAl can lead to dras-

tic alterations of its magnetic properties⁵. Furthermore, X-ray studies revealed that hydrogenation (deuteration) is accompanied by orthorhombic distortion of the hexagonal ZrNiAl-type structure, adopted by pure TbNiAl, but the location of H (D) atoms in the crystal lattice remained unknown. On the other hand, UNiAl displays a variety of interesting phenomena, such as magnetic order and heavy fermion behaviour⁶. This compound is close to the magnetic border due to large delocalization of the 5f electrons. Generally, it is accepted that 5f-ligand hybridization is responsible for this delocalization. Hydrogenation/ deuteration of pure UNiAl affects this mechanism simply because of the changes in the interatomic distances. Hydrogenation/deuteration is also accompanied by drastic changes in the magnetic properties⁷.

Here we report on the crystal and magnetic structures of TbNiAl and UNiAl hydrides and deuterides studied by means of neutron diffraction.

Samples were prepared by arc melting. Several remeltings were done in order to achieve high homogeneity. Crystal structure of the obtained compound had been checked by X-ray analysis, which confirmed that it was a single-phase TbNiAl and UNiAl polycrystals. Hydrides (deuterides) were obtained as follows: first, the intermetallic compound was crushed and activated in the high vacuum of $\sim 10^{-6}$ Torr at 350 °C for 1 hour, afterwards it was cooled down to room temperature and exposed to H (D) at 10 atm pressure. Amount of absorbed H was determined by monitoring decrease of pressure in the calibrated volume. In order to obtain the lower deuteride, the saturated sample was heated up to 155 °C and kept at this temperature until pressure has stabilized. Then the reaction chamber was disconnected from the hydrogenation system and cooled down to the room temperature. X-ray analysis was used to check to quality of the resulting compounds.

For the neutron diffraction experiments, powder samples of TbNiAlD_{1.28}, TbNiAlD_{0.8} and UNiAlD_{2.23} were ground and sealed in vanadium tubes under helium atmosphere. Diffraction data were taken at various temperatures between 4 and 300 K using the powder diffractometers NPD and HIPD at the Manuel Lujan Jr. Neutron Scattering Center and the powder diffractometer HIPD at the Intense Pulsed Neutron Source. NPD is a high-resolution diffractometer, used for crystal-structure refinements, with 4 detector banks covering d-spacings up to 4 Å, while both

HIPD are a high-intensity diffractometers, well suited for magnetic-structure refinements, covering a range up to 20 Å. The data were analyzed by using the Rietveld-refinement program package GSAS⁸.

Our Rietveld refinements on TbNiAlD_{1.28} and TbNiAlD_{0.8} indicate that both compounds form in the base-centered orthorhombic space group Amm2 (No 38), with structural parameters as given in Tables I and II, respectively. Atom fractions of Tb, Ni and Al were found to be very close to the exact 1:1:1 stoichiometry, and we subsequently refined only the D fractions in the two samples. The resulting structure is shown on the Figure 1.

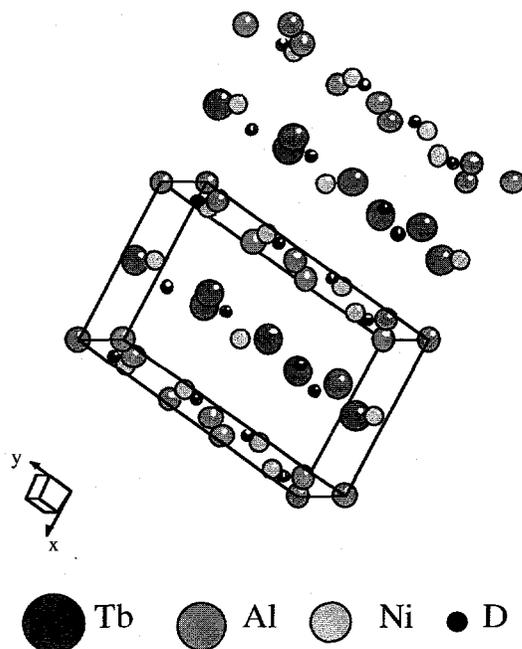


Fig.1 Crystal structure at room temperature of TbNiAlD_{1.28} and TbNiAlD_{0.8} (main phase).

Table I: Refined structural parameters for TbNiAlD_{1.28}

| Atom | Site | x | y | z | % fraction |
|-------|------|-----|------------|-------------|------------|
| Tb(1) | 4e | 0.5 | 0.2096 (2) | 0.0434 (3) | 100 |
| Tb(2) | 2b | 0.5 | 0 | 0.6550 (4) | 100 |
| Ni(1) | 4d | 0 | 0.3319 (2) | 0.2751 (3) | 100 |
| Ni(2) | 2b | 0.5 | 0 | 0.2481 (3) | 100 |
| Al(1) | 4d | 0 | 0.1179 (4) | 0.3339 (6) | 100 |
| Al(2) | 2a | 0 | 0 | 0 | 100 |
| D(1) | 4e | 0.5 | 0.3330 (3) | 0.2628 (6) | 98±1 |
| D(2) | 4d | 0 | 0.3834 (3) | 0.07775 (4) | 94±1 |

a=3.73422(7)Å, b=12.3667(3)Å, c=7.6277(2)Å;

R_{wp} = 4.8%; R_p = 3.5%; Reduced χ^2 = 1.7.

The diffraction data on the second sample (which had a nominal composition of about TbNiAlD_{0.8}) indicate the formation of two phases with quite different lattice parameters. The structure of the main phase is found to be closely related to those of TbNiAlD_{1.28} (Table II) with the D occupying positions in the x=0 and x=1/2 planes only. For the 'impurity phase' on the other hand, we have indications that the D atoms are located between those planes. The structure of the main phase (TbNiAlD_{0.81}) is the same as the one shown in Figure 1. For both phases, we find that only a fraction of the D positions are occupied (see Table II).

For both samples, magnetic ordering sets in at low temperatures. In TbNiAlD_{1.28} the HIPD data revealed two extra peaks at 7.21 and 12.90 Å, which occur below 16 K. These reflections are magnetic in origin and can be indexed in the Amm2 cell with doubled *a* and *b* axis, indicating a magnetic propagation vector of $\mathbf{q} = (1/2, 1/2, 0)$. Similarly, in the biphasic sample

(TbNiAlD_{0.8}), magnetic reflections are seen at the 20 K NPD data, which are absent at room temperature. Closer inspection reveals that some magnetic contributions can be indexed assuming a cell doubling of *a* and *b* axis of the main phase, where the D atoms occupy x=0 and x=1/2 positions.

Table II: Refined structural parameters of TbNiAlD_{0.8}, main (phase 1) and 'impurity' (phase 2) phases, at room temperature.

| Phase | Atom | Site | x | y | z | % fraction |
|-------|-------|------|-----|------------|-----------|------------|
| 1 | Tb(1) | 4e | 0.5 | 0.211 (4) | 0.027 (2) | 100 |
| | Tb(2) | 2b | 0.5 | 0 | 0.636 (2) | 100 |
| | Ni(1) | 4d | 0 | 0.3286 (4) | 0.205 (2) | 100 |
| | Ni(2) | 2b | 0.5 | 0 | 0.231 (2) | 100 |
| | Al(1) | 4d | 0 | 0.125 (1) | 0.335 (3) | 100 |
| | Al(2) | 2a | 0 | 0 | 0 | 100 |
| | D(1) | 4e | 0.5 | 0.322 (1) | 0.217 (3) | 81±1 |
| | D(2) | 4d | 0 | 0.346 (1) | 0.015 (3) | 44±2 |
| 2 | Tb(1) | 4e | 0.5 | 0.2069 (4) | 0.052 (4) | 100 |
| | Tb(2) | 2b | 0.5 | 0 | 0.659 (4) | 100 |
| | Ni(1) | 4d | 0 | 0.3339 (7) | 0.249 (3) | 100 |
| | Ni(2) | 2b | 0.5 | 0 | 0.247 (3) | 100 |
| | Al(1) | 4d | 0 | 0.117 (3) | 0.353 (1) | 100 |
| | Al(2) | 2a | 0 | 0 | 0 | 100 |
| | D(1) | 8f | | | | 44.0±0.4 |
| | D(2) | 8f | | | | 16.7±0.7 |

Phase 1: a = 3.8396(1) Å, b = 12.4571(6) Å, c = 7.2877(4) Å;

Phase 2: a = 3.91174(8) Å, b = 12.3524(8) Å, c = 7.1206(4) Å;

R_{wp} = 10%; R_p = 7%; Reduced χ^2 = 12

In the case of UNAlD_{2.23}, the nuclear peaks could be indexed on the same hexagonal structure as that of UNiAl, i.e. P-62m (No. 189). The lattice constants *a* and *c* are 7.1916(3) and 3.9956(3) Å re-

spectively. Compared to UNiAl before hydrogenation, the lattice is 6.8% elongated along the a axis and 1% contracted along the c axis.

Rietveld analysis shows the U atoms moving further to $(2/3, 0, 1/2)$ and the Al to $(1/3, 0, 0)$. Such re-arrangement makes the 3g site more favorable for D occupation and creates additional D sites at 2e and 4h. The following interstitial sites in the space group P-62m were taken into account: 3g $(1/3, 0, 1/2)$, 2e $(0, 0, 1/2)$, 4h $(1/3, 2/3, 0.40)$ and 3f $(0.72, 0, 0)$. The best fit was achieved when the 3g site was fully occupied, and the 2e and 4h sites were 81% and 40% occupied, respectively.

At low temperatures, additional magnetic reflections are observed. At 50 K, we observe a magnetic reflection at about 3.2 Å. At 4.2K, on the other hand, weak satellites and a second magnetic reflection evolves at about 2 Å. Analysis of the magnetism in UNiAlD_{2.23} is presently underway.

These findings provide evidence that D may occupy different positions in the crystal lattice, and magnetic properties of the material are strongly dependent on the location of those atoms^{5,7}. The location of D (H) in these materials seems to be extremely sensitive to small differences in such conditions, as sample preparation, aging, etc⁹. This may explain recent bulk magnetic results, where different behavior was reported for some

TbNiAl deuterides and hydrides with equal nominal compositions⁵. Furthermore, our neutron results indicate a ratio between main and impurity phases of TbNiAlD_{0.8} of about 3:1, while X-rays performed some few months earlier indicated a phase ratio of 10:1 only¹⁰. This may indicate that (some of) the phases are not stable enough and decomposition or phase transformation may influence the properties in addition. A detailed study of samples with different history is required.

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