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Journal of Alloys and Compounds 404–406 (2005) 200–203

Journal of ALLOYS AND COMPOUNDS

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# Crystal and magnetic structure of $HoNiSnD_{0.67}$

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Received 1 June 2004; received in revised form 6 September 2004; accepted 15 September 2004
Available online 14 July 2005

**Abstract**

Crystal and magnetic structure and magnetic properties for deuteride $HoNiSnD_{0.67}$ are provided on the basis of high-resolution powder X-ray and neutron diffraction and magnetometric data. This deuteride crystallises with the hexagonal ZrNiAl type related structure and is antiferromagnetic below the Néel temperature equal to 2.6(3) K. The deuterium atoms occupy the tetrahedral 4h $Ho_3Ni$ sites. At 2 K Ho magnetic moments form a sine-modulated magnetic structure described by the propagation vector **k**(= 0.34, 0.34, 0.117). The Ho magnetic moment, equal to $5.36\mu_B$, lies in the basal plane (0 0 1).


*Keywords:* Hydrides; Powder neutron diffraction; Magnetic structure

## 1. Introduction

Recently, several studies have been devoted to the hydrogenation of RTX intermetallics (R= rare earth element, T= nd transition element and X=p-element). In all cases the insertion of hydrogen in the metal lattice induces changes in the crystal or electronic structures.

The present work aims on studies of the influence of deuteration on the crystal and magnetic structure and magnetic properties of HoNiSn. The HoNiSn compound crystallises in the orthorhombic TiNiSi-type structure and is antiferromagnetic with the Néel temperature equal to 3.0 K [1]. Neutron diffraction data show that at $T = 1.4$ K HoNiSn has sine-modulated magnetic structure with the wave vector **k**(= 0.3593, 0.3337, 0). The holmium magnetic moment, equal to $8.5\mu_B$, lies in the (a, b) plane and forms the angle of 75° with the *a*-axis [2]. The deuteration of HoNiSn leads to the formation of $HoNiSnD_{0.67}$ and results in a structural phase transition from the TiNiSi-type orthorhombic structure to the ZrNiAl-type hexagonal one leading to the unusual effect of volume contraction on hydrogenation [3]. Deuterium atoms in $HoNiSnD_{0.67}$ fill every second available $Ho_3Ni$ tetrahedral site.

In present work the results of the X-ray and neutron diffraction and magnetic measurements of a polycrystalline sample of $HoNiSnD_{0.67}$ are presented. From these data the magnetic structure of this compound is determined.

## 2. Experimental detail

HoNiSn intermetallic alloy was prepared from high purity constituent elements, by arc melting under argon gas atmosphere. X-ray diffraction diagrams (Siemens D 5000 diffractometer, Cu K$\alpha_1$ radiation, Bragg-Brentano geometry) showed a formation of the equiatomic intermetallic compound crystallizing with the TiNiSi type structure with no visible impurities present.

In further studies, the alloy was used in as cast condition. Deuteration was performed in a stainless steel autoclave at deuterium pressure of 1–2 bar and temperatures 400–450 °C.

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doi:10.1016/j.jallcom.2004.09.087

Synthesis resulted in the formation of $HoNiSnD_{0.67\pm0.05}$. After completion of the $D_2$ absorption, the autoclave with the sample was slowly cooled in a furnace to room temperature. Powder neutron diffraction (PND) data of $HoNiSnD_{0.67}$ (sample was sealed under argon in a 5 mm vanadium sample holder) were measured on the D1B instrument ($\lambda = 2.52$ Å), ILL, at 230 and 2 K using the ILL type yellow cryostat. This diffractometer is equipped with a multidetector (400 cells) system covering an angular $2\theta$ range of 80° with a step of 0.2°. Further details describing the powder neutron diffraction instrument used can be found in the ILL yellow book available at the http://www.ill.fr. The refinements of the data were performed using the GSAS software [4] and the following neutron scattering lengths taken from the GSAS library: $b_{Ce} = 4.84$ fm, $b_{Ni} = 10.20$ fm, $b_{Ho} = 8.01$ fm, $b_{Sn} = 6.23$ fm, $b_D = 6.67$ fm. XRD data for the deuteride were collected at the high resolution diffractometer accommodated at SNBL, ESRF (monochromatic X-rays with $\lambda = 0.50056$ Å). These data showed that a small fraction of the sample remained undeuterated during the process of interaction with deuterium.

The GSAS [4] program was used in the refinements of the nuclear structure from powder diffraction data. The FULLPROF program [5] was employed in the evaluation of the magnetic ordering.

The magnetic measurements have been recorded by the extraction method [6] in a continuous field of 0.01, 0.1 and 1 T. A detailed description of the experimental set up can be found elsewhere [6].

## 3. Results

The temperature dependence of the magnetic susceptibility indicates that $HoNiSnD_{0.67}$ is an antiferromagnet with the Néel temperature 2.6(3) K (see inset in Fig. 1). Above the Néel temperature the magnetic susceptibility obeys the Curie–Weiss law with a negative value of the paramagnetic Curie temperature equal –4 K and the effective magnetic moment equal $10.93\mu_B$ which is close to the value for the $Ho^{3+}$ ion ($10.61\mu_B$). This demonstrates that no contribution from the Ni atoms to the magnetic (Curie–Weiss) behaviour is observed.

Analysis of the X-ray (see Fig. 2) and neutron diffraction data in paramagnetic state collected at 293 and 230 K, respectively, showed that the studied sample contains two phases: $HoNiSnD_{0.67}$ (84%) and undeuterated intermetallic HoNiSn (16%). Results of the Rietveld refinements of the synchrotron XRD and PND are listed in Table **??**. Fig. 4 shows the crystal structure of the $HoNiSnD_{0.67}$ with deuterium atoms located in the $Ho_3Ni$ tetrahedra.

The additional reflections of magnetic origin, observed on the neutron diffraction pattern at 2 K (see Fig. 3) are indexed by the propagation vector $k_1(= 0.34, 0.34, 0.117)$ for $HoNiSnD_{0.67}$ and $k_2(= 0.395, 0.330, 0)$ for HoNiSn. The Ho magnetic moment associated with $k_1$ is equal to $5.36(5)\mu_B$,

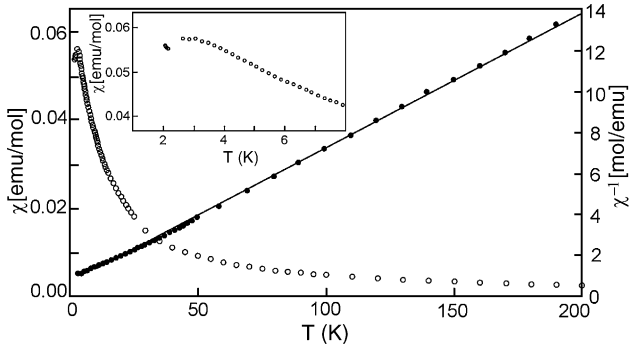


Fig. 1. Temperature dependence of the magnetic susceptibility and reciprocal magnetic susceptibility of $HoNiSnD_{0.67}$. The inset shows the low temperature dependence of the magnetic susceptibility.

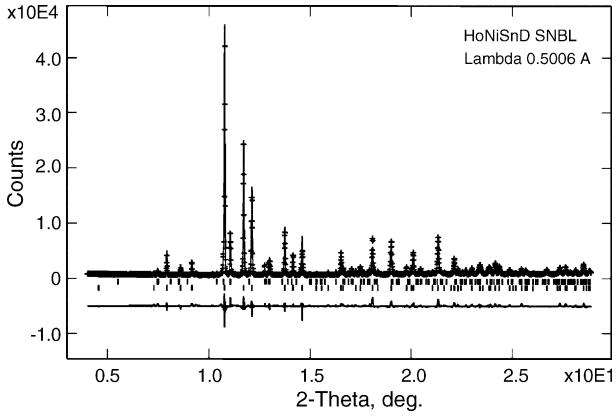


Fig. 2. Powder diffraction pattern for the $HoNiSnD_{0.67}$ intermetallic compound (synchrotron radiation, $\lambda = 0.50056$ Å).

lies in the basal plane (0 0 1) and forms a sine modulated structure (see Fig. 5). The three moments in the crystal unit cell, $S_1(x, 0, 1/2)$, $S_2(0, x, 1/2)$ and $S_3(\bar{x}, \bar{x}, 1/2)$ form non-collinear order.

The magnetic structure of HoNiSn is similar to those determined in Ref. [2]. The Ho magnetic moments in the crystal

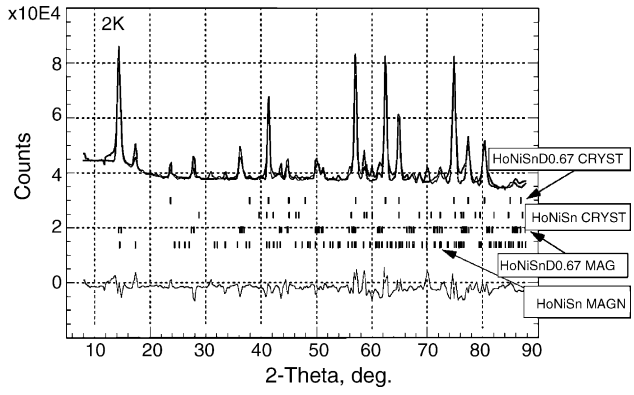


Fig. 3. Observed and calculated neutron diffraction patterns of $HoNiSnD_{0.67}$ at 2 K. Circles represent the experimental data, solid lines are for the calculated profile and at the bottom the difference between the observed and calculated data is shown. Vertical bars indicate the nuclear and magnetic peaks.

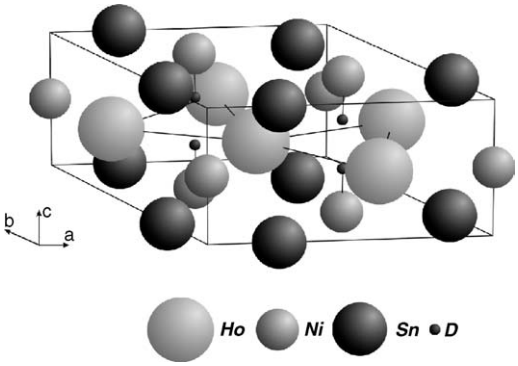


Fig. 4. Crystal structure of $HoNiSnD_{0.67}$.

unit cell $S_1(x, 1/4, z)$, $S_2(\bar{x}, 3/4, \bar{z})$, $S_3(1/2 - x, 3/4, 1/2 + z)$ and $S_4(1/2 + x, 1/4, 1/2 - z)$ are ordered with the sequence + + −−. The Ho moments equal to $8.27\mu_B$ lie in the (a, b) plane and form an angle of 75° with the *a*-axis.

## 4. Discussion and summary

The results of our X-ray and neutron diffraction work confirm that the deuteration caused a change of the crystal structure from orthorhombic TiNiSi-type to the hexagonal ZrNiAl-type and a small decrease of the volume, −0.64%. In $HoNiSnD_{0.67}$ deuteride the deuterium atoms occupy with 50% probability the site 4h. The atomic structure of $HoNiSnD_{0.67}$ is isostructural with chemically similar lower deuterides $RNiInD_{0.5–0.6}$ formed by La and Nd [7]. Interatomic distances in the $HoNiSnD_{0.67}$ within the filled by D $Ho_3Ni$ tetrahedronare: Ho–D, 2.23(1) Å; Ni–D, 1.67(7) Å.

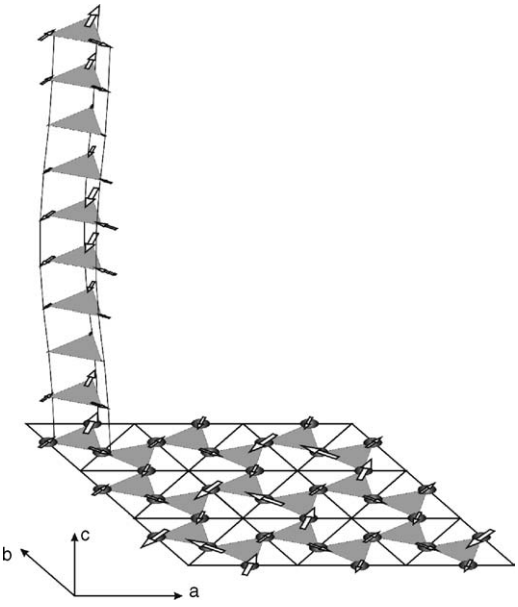


Fig. 5. Magnetic structure of $HoNiSnD_{0.67}$.

Table 1
Crystal structure parameters of the $HoNiSnD_{0.67}$ and HoNiSn compounds at 293 K from the X-ray synchrotron radiation and 230 K from neutron diffraction data

| X-ray diffraction, $T = 293$ K | Neutron diffraction, $T = 230$ K |
|---|---|
| $HoNiSnD_{0.67}$ (ZrNiAl-type) | ($P\bar{6}2m$ space group) |
| The atoms occupy the following positions: | |
| Ho atoms in 3g site: $x_1$, 0, 1/2; 0, $x_1$, 1/2; $\bar{x}_1$,$\bar{x}_1$, 1/2 | |
| Ni atoms in 1b site: 0, 0, 1/2 and 2c site: 1/3, 2/3, 0; 2/3, 1/3, 0 | |
| Sn atoms in 3f site: $x_2$, 0, 0; 0, $x_2$, 0; $\bar{x}_2$, $\bar{x}_2$, 0 | |
| D atoms in 4h site: 1/3, 2/3, z; 1/3, 2/3, $\bar{z}$ ; 2/3, 1/3, z; 2/3 1/3, $\bar{z}$ | |
| $a = 7.24197(10)$ Å, $b = 7.24197(10)$ Å | $a = 7.2402(20)$ Å, $b = 7.2402(20)$ Å, |
| $c = 3.93514(7)$ Å | $c = 3.9360(13)$ Å |
| $x_1$(Ho) = 0.5934(3) | $x_1$(Ho) = 0.5984(21) |
| $x_2$(Sn) = 0.2633(3) | $x_2$(Sn) = 0.2587(23) |
| | $z(D) = 0.577(18)$ |
| HoNiSn (TiNiSi-type) | (*Pnma* space group) |
| The 4c sites: | |
| $x$, 1/4, $z$; $\bar{x}$, 3/4, $\bar{z}$; $1/2 - x$, 3/4, $1/2 + z$; $1/2 + x$, 1/4, $1/2 - z$; | |
| are occupied by four Ho, four Ni and four Sn atoms, each with different $x$ and $z$ parameters | |
| Ho: $x = 0.4924$, $z = 0.2992$ | $x = 0.459(20)$, $z = 0.306(21)$ |
| Ni: $x = 0.2955$, $z = 0.5834$ | $x = 0.197(17)$, $z = 0.551(23)$ |
| Sn: $x = 0.8079$, $z = 0.5871$ | $x = 0.816(27)$, $z = 0.570(40)$ |

All D–D distances are larger than 2 Å (only one site of a pair separated by 0.60(14) Å is occupied by D leaving the other position empty).

In both compounds, HoNiSn and $HoNiSnD_{0.67}$, the Ho magnetic moments form a sine-modulated magnetic structure. Deuteration retains practically unchanged the Néel temperature (3 and 2.6(3) K). However, it reduces the Ho magnetic moment from $8.27(7)\mu_B$ for HoNiSn to $5.36(5)\mu_B$ for $HoNiSnD_{0.67}$, and alters the direction of the magnetic moments. In HoNiSn it is practically perpendicular to the (0 1 0) plane in which lie the Ho atoms. In contrast, in $HoNiSnD_{0.67}$ Ho moments are confined to the (0 0 1) plane of Ho atoms. This alteration can be associated with the location of the shortest Ho-Ho interatomic distances, 3.613 and 3.789 Å in HoNiSn, and 3.806 and 3.935 Å in $HoNiSnD_{0.67}$ (further details are required).

The results of the calculation of the electronic structure of $RNiInD_x$ (R= La, Ce, Pr, Nd) compounds indicate degeneration in the energy states H 1s and R 4f which implies a possible covalent bonding contribution of the R–H and Ni–H bond [8].

## Acknowledgment

We are grateful to Mr. Gondek for discussion.

## References

[1] Y. Andoh, M. Kurisu, S. Kawano, I. Oguro, J. Magn. Magn. Mater. 177–181 (1998) 1063.
[2] J.A. Yakinthos, Ch. Routsi, J. Magn. Magn. Mater. 149 (1995) 273.
[3] V.A. Yartys, O. Isnard, A.B. Riabov, L.G. Akselrud, J. Alloys Compd. 356–357 (2003) 109.
[4] A.C. Larson, R.B. von Dreele, General Structure Analysis System (GSAS), LANSCE MS-H, 805, 1994.
[5] J. Rodriguez-Carvajal, Physica B 192 (1993) 55.
[6] A. Barlet, J.C. Genna, P. Lethuillier, Cryogenics 31 (1991) 801.
[7] V.A. Yartys, R.V. Denys, B.C. Hauback, H. Fjellvåg, I.I. Bulyk, A.B. Riabov, Ya.M. Kalychak, J. Alloys Compd. 330–332 (2002) 132.
[8] P. Vajeeston, P. Ravindran, R. Vidye, A. Kjekshus, H. Fjellvåg, V.A. Yartys, Phys. Rev. B 67 (2003) 014101.