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Journal of Alloys and Compounds 356–357 (2003) 65–68

Journal of ALLOYS AND COMPOUNDS

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In situ powder neutron diffraction study of $LaNiInD_{1.63}$ with short D . . . D distances

R.V. Denys[a], A.B. Riabov[a], V.A. Yartys[b,*], B.C. Hauback[b], H.W. Brinks[b]

[a]*Physico-Mechanical Institute of the National Academy of Sciences of Ukraine, 5 Naukova St., 79601 Lviv, Ukraine*
[b]*Institute for Energy Technology, P.O. Box 40, Kjeller N-2027, Norway*

Received 26 August 2002; accepted 15 November 2002

Abstract

The recent powder neutron diffraction study of the crystal structure of $LaNiInD_{1.22}$ [J. Alloys Comp. 330–322 (2002) 132] concluded on the formation of a D . . . D pair with an unusually short interatomic distance of 1.63 Å. Hydrogen atoms in $LaNiInD_{1.22}$ occupy a single crystallographic site and are coordinated by face-sharing La_3Ni tetrahedra (92% occupancy). PCT measurements show that hydrogen storage capacity of LaNiIn, 1.63 at.H/formula unit, exceeds the limit of 1.33 at.H/LaNiIn when the La_3Ni sites are completely occupied. In the present work, in situ powder neutron diffraction data were collected under D_2 pressure of 4.6 bar in order to study the deuteride with a maximum D content in the metal matrix. In the hexagonal structure of $LaNiInD_{1.63}$ (space group $P\bar{6}2m$; $a=7.3874(4)$; $c=4.6816(2)$ Å) Rietveld refinements showed that deuterium atoms occupy 36% of the available distorted La_3NiIn_2 octahedra, in addition to the 96% filled La_3Ni sites. The structure of $LaNiInD_{1.63}$ represents the first example of a deuteride containing direct In–D bonds (2.346(2) Å). H bonding to the La_3NiIn_2 sites is rather weak and a desorption from these sites takes place at room temperature and hydrogen pressures below 1 bar.

Keywords: Metal hydrides; Neutron diffraction; Gas–solid reactions; Crystal structure

1. Introduction

$RNiInD_{\sim 1.2}$ (R = La, Ce, Nd) hydrides represent a new type of metal hydrides containing H . . . H pairs with short interatomic distance of 1.56–1.63 Å [1]. The violation of the well known 'rule of 2 Å' [2] occurring in the $RNiInH(D)_{1.2}$ hydrides attracts further interest to the studies of the $RNiIn–H_2$ systems.

Hydrogen atoms in $RNiInD_{\sim 1.2}$ occupy trigonal bipyramids R_3Ni_2 with a double occupancy. One D atom is inside each R_3Ni tetrahedron. The R_3Ni tetrahedra share common triangular faces R_3 and thus form a closely distanced pair of H atoms. A complete filling of the R_3Ni tetrahedra gives a maximum H storage capacity of 1.33 at. H/RNiIn. This value is lower than the data obtained by the volumetric measurements at pressure of 100 bar H_2 [3] and from PCT measurements in the $RNiIn–H_2$ systems [4], both giving 1.6–1.7 at.H/f.u. The difference originates from the ex situ type of measurements performed in Ref. [1] during the powder neutron diffraction (PND) experiment. Therefore, it is evident that the saturated deuteride partially releases deuterium during preparation for the PND measurements. This work aims at the study of the crystal structure of the saturated deuteride $LaNiInD_{1.6-1.7}$ by in situ PND experiment in deuterium gas in order to prevent deuterium release from the metal matrix.

2. Experimental

The LaNiIn intermetallic alloy was prepared by argon arc melting of the mixture of the constituent elements, La, Ni and In, with purity not less than 99.9%. Lanthanum was taken with excess of 1 at.% in order to compensate evaporation during the melting. The as-cast alloy was annealed at 600 °C in an evacuated quartz tube for 4 weeks and thereafter quenched into the ice water. From powder X-ray diffraction study (PXD) it was confirmed that the LaNiIn intermetallic compound was the only constituent

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*Corresponding author. Tel.: +47-63-806-453; fax: +47-64-812-905.
E-mail address: volodymyr.yartys@ife.no (V.A. Yartys).

0925-8388/03/$ – see front matter
doi:10.1016/S0925-8388(03)00101-4

(hexagonal; space group $P\bar{6}2m$; $a = 7.5906(9)$; $c = 4.050(1)$ Å).

PND data were collected with the PUS diffractometer accommodated at JEEP II reactor (Kjeller) under the following experimental conditions: $\lambda = 1.5554$ Å; focusing Ge (511) monochromator; position sensitive detector; $2\theta = 10–130°$; $\Delta 2\theta = 0.05°$; 2400 data points. The sample was kept in a silica-glass tube with a diameter of 6 mm. The tube was placed into a tantalum furnace and formed a part of the Sieverts type system allowing an application of vacuum or D_2 pressures up to 10 bar to the sample. Before the experiment the LaNiIn alloy (~1.5 g) was ground into coarse powder. The alloy was activated for 30 min in vacuum at 400 °C. After cooling the sample to room temperature, deuterium gas at a pressure of 4.6 bar was introduced into the system. The system was refilled with D_2 until the equilibrium concentration of deuterium was reached. A small part of the alloy remained non-deuterated under the conditions of the experiment and was introduced into the refinements of the PND data as a secondary phase. D content in the deuteride, D/LaNiIn = 1.63±0.05, was estimated from the volumetric data of deuterium absorption and was corrected for the amount of non-deuterated LaNiIn (9.83(9) wt.%).

The PND data were refined using the General Structure Analysis System (GSAS) software [5]. Nuclear scattering lengths were taken from the GSAS library: $b_{La} = 8.27$; $b_{Ni} = 10.30$; $b_{In} = 4.06$; $b_D = 6.67$ fm. The Ta heating coil of the furnace gave five extra diffraction peaks in the PND diagram. The angle ranges covering these peaks were excluded from the refinements. Diffuse peaks of neutron scattering around 2θ ~20°, ~43° ~80° were from the quartz sample holder. They were modelled using a non-linear background with a cosine Fourier series polynomial.

3. Results and discussion

The PND pattern of $LaNiInD_{1.63}$ was indexed on a hexagonal unit cell with parameters $a = 7.3874(4)$, $c = 4.6816(2)$ Å, slightly higher than for the deuteride with the lower D content, $LaNiInD_{1.22}$ [1], $a = 7.3810(4)$, $c = 4.6489(3)$ Å. Available interstitial positions for the accommodation of deuterium atoms in $LaNiInD_{1.63}$ were located by crystal chemistry analysis. The summary of this analysis is presented in Table 1. Table 1 shows that there is only one type of site formed by La and Ni atoms, La_3Ni1 tetrahedra 4*h*. Those sites are occupied by D atoms in $LaNiInD_{1.22}$. All other interstices have indium atoms in their surroundings. The 6*i* and 2*e* tetrahedra seem to be too small for the insertion of H atoms with radii less than 0.4 Å. From size consideration, a pentagonal bipyramid 3*f* $La_2Ni1_2In_3$ ($r = 0.45$ Å), a distorted octahedron 3*g* La_3Ni2In_2 ($r = 0.63$ Å) and a tetrahedron 12*l* La_2Ni1In ($r = 0.40$ Å) appear to be preferable interstitial sites for H atoms in addition to the 4*h* La_3Ni1 ($r = 0.47$ Å) tetrahedra. From a chemical surroundings point of view the octahedron La_3Ni2In_2 and a tetrahedron La_2Ni1In containing 50% of La atoms are the most preferable options. The pentagonal bipyramid $La_2Ni1_2In_3$ is less favourable because of the smaller amount of rare earth metal (2/7) and the higher relative amount of indium atoms (3/7) in its surrounding. The complete filling of either 3*g* or 3*f* sites together with 4*h* sites increases H-storage capacity to 2.33 at.H/f.u. The highest possible capacity with two completely filled sites is reached with simultaneous occupation of the 12*l* and 4*h* sites (5.33 at.H/f.u.). In all these cases the experimentally observed H storage capacity of 1.6–1.7 at.H/f.u. [2] is exceeded. A joint occupancy of three or more sites is also possible.

Table 1
Interstices in the crystal structure of $LaNiInH_{1.22}$

Site		Coordinates			r_i, Å	Neighbours
		x	*y*	*z*		
4*h*[a]	La_3Ni1	2/3	1/3	0.369	0.47	4*h*; 3 × 12*l*
12*l*	La_2Ni1In	0.301	0.804	0.748	0.40	4*h*; 3*g*; 2 × 3*f*
6*i*	$LaNi2In_2$	0.856	0	0.744	0.31	2*e*; 3*f*; 2 × 3*g*
2*e*	$Ni2In_3$	0	0	0.168	0.30	2*e*; 3 × 6*i*
3*g*	La_3Ni2In_2	0.260	0	1/2	~0.63	4 × 12*l*; 4 × 6*i*
3*f*	$La_2Ni1_2In_3$	0.604	0	0	0.45[b]	8 × 12*l*; 2 × 6*i*

Space group $P\bar{6}2m$; $a = 7.3810(4)$; $c = 4.6489(3)$ Å. 3 La in 3*g*: *x*, 0, 1/2 ($x = 0.6035$); 2 Ni1 in 2*c*: 1/3, 2/3, 0; 1 Ni2 in 1*b*: 0, 0, 1/2; 3 In in 3*f*: *x*, 0, 0 ($x = 0.2437$); 3.68 D in 4*h*: 1/3, 2/3, *z* ($z = 0.6759$).

[a] D-filled in the structure of $LaNiInD_{1.22}$ site.

[b] Axial radius.

Rietveld profile refinements of the in situ powder neutron diffraction data (Fig. 1) showed an increased occupation of the 4*h* sites, for $LaNiInD_{1.63}$ compared to $LaNiInD_{1.22}$ (96% and 92%, respectively). The short D . . . D separations are therefore also present in the structure of $LaNiInD_{1.63}$. An additional site occupied by D atoms was found by a difference Fourier analysis (Fig. 2). Additional maxima of nuclear density were located inside the La_3Ni2In_2 octahedra. These maxima are nonspherical in shape and are elongated towards two La atoms. Anisotropic displacement parameters for the deuterium atoms were introduced into the refinements in order to properly account for this elongation. The results of the refinement are given in Table 2. Interatomic distances for the $LaNiInD_{1.63}$ are listed in Table 3, and the structure is shown in Fig. 3.

The large anisotropy in the displacement parameters for D2 indicating disorder/hopping into the four tetrahedral La_2Ni2In sites ($4{*}La_2Ni2In = La_3Ni2In_2$ octahedron) separated by about 0.35 Å. However, from the Rietveld refinements it was concluded that D2 was in the center of the octahedron. Further studies are necessary to determine the behaviour of H in $LaNiInH(D)_{1.63}$ in more detail.

The main differences between the structures of $LaNiInD_{1.63}$ and $LaNiInD_{1.22}$ are:

(a) the unit cell dimensions increase slightly on the transition from $LaNiInD_{1.22}$ to $LaNiInD_{1.63}$. The lat-

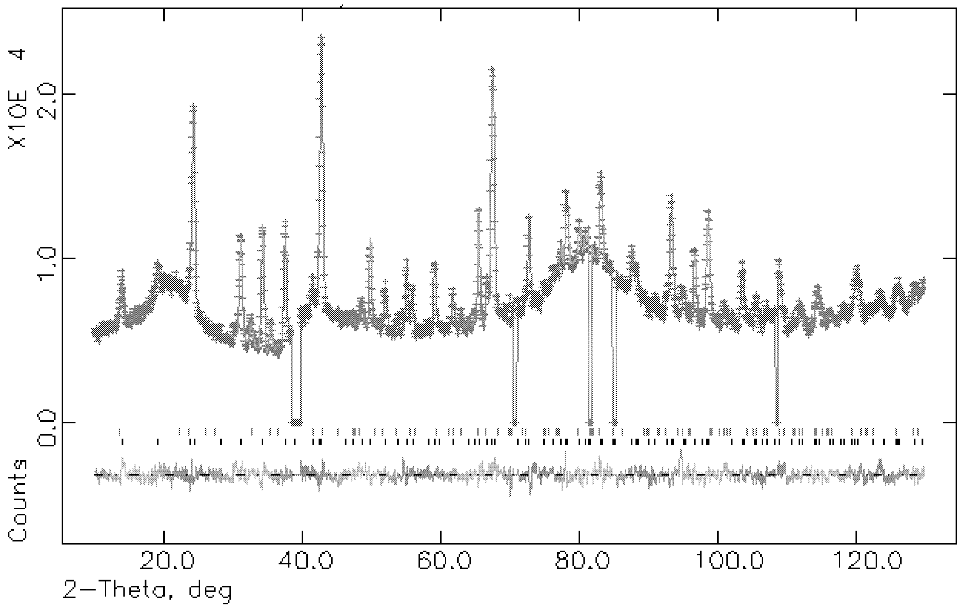

Fig. 1. In situ PND pattern of the $LaNiInD_{1.63}$ deuteride (25 °C, PUS diffractometer, $\lambda=1.5554$ Å, $R_p=3.09\%$, $R_{wp}=4.04\%$). Experimental (+), calculated (upper line) and difference (lower line) profiles and positions of the Bragg's peaks for $LaNiInD_{1.63}$ (below) and LaNiIn (upper) are shown. The excluded intervals of 2θ cover the regions of the reflections from the tantalum furnace.

tice expansion along c, $\Delta c/c$, is higher for the $LaNiInD_{1.63}$ (~16%) than for $LaNiInD_{1.22}$ (~15%). The anisotropy of the unit cell expansion reflected by the c/a ratio is nearly the same for both deuterides (LaNiIn: 0.533; $LaNiInD_{1.22}$: 0.630; $LaNiInD_{1.63}$: 0.634);

(b) the D1 . . . D1 interatomic distance is ~6% longer in the saturated deuteride $LaNiInD_{1.63}$ compared to $LaNiInD_{1.22}$ (1.715 and 1.635 Å, respectively);

(c) the Ni1 . . . D1 distance is short and close to the sum of the covalent radii (1.47 Å [6]) for both $LaNiInD_{1.22}$ (1.507 Å) and $LaNiInD_{1.63}$ (1.494 Å);

(d) D2 atoms in the $3g$ sites are far distanced from both D1 (3.06(1) Å) and from the same type D2 atoms (2.89(2) Å);

(e) the large size of the La_3Ni2In_2 site and the presence of

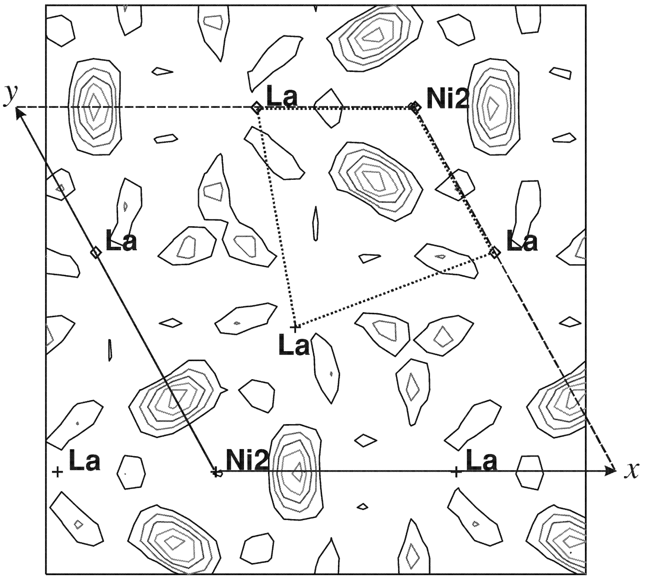

Fig. 2. Difference Fourier synthesis map of the residual nuclear density (cross section in the {001} plane at $z=1/2$) for $LaNiInD_{1.63}$. Observed maxima give the positions of the D2 atoms. The boundaries of the unit cell and the equatorial plane of the deformed octahedron La_3Ni2In_2 are outlined by a dashed line.

Table 2
Atomic coordinates, displacement parameters (U_{ISO}), and site occupancies for the structure of the $LaNiInD_{1.63}$ deuteride (space group $P\bar{6}2m$; $a=7.3874(4)$; $c=4.6816(2)$ Å)

Atom	Site	x	y	z	Occupancy	$U_{iso}\times100$ Å^2
La	$3g$	0.6030(6)	0	1/2	1.0(–)	0.9(1)
Ni1	$2c$	1/3	2/3	0	1.0(–)	1.4(1)
Ni2	$1b$	0	0	1/2	1.0(–)	1.0(1)
In	$3f$	0.247(1)	0	0	1.0(–)	0.5(2)
D1	$4h$	1/3	2/3	0.317(1)	0.96(1)	2.3[a]
D2	$3g$	0.226(3)	0	1/2	0.36(2)	9.4[a]

[a] Equivalent isotropic displacement parameters.

Table 3
Interatomic distances in the structure of $LaNiInD_{1.63}$

Atoms	δ, Å	Atoms	δ, Å	Atoms	δ, Å
La–4La	3.922(3)	Ni2–3La	2.933(5)	D1–3La	2.421(3)
–2Ni1	3.257(1)	–6In	2.969(5)	–Ni1	1.494(6)
–Ni2	2.933(5)	–3D2	1.67(1)	–D1	1.715(1)
–2In	3.520(7)	In–2In	3.520(7)	–3D2	3.06(1)
–4In	3.473(3)	–2La	3.473(3)	D2–La	2.79(1)
–4D1	2.421(3)	–2Ni1	2.835(5)	–2La	2.548(4)
–D2	2.79(1)	–2Ni2	2.969(5)	–Ni2	1.67(1)
–2D2	2.548(4)	–2In	3.16(1)	–2In	2.346(2)
Ni1–6La	3.257(1)	–2D2	2.346(2)	–4D1	3.06(1)
–3In	2.835(5)			–2D2	2.89(2)
–D1	1.494(6)				

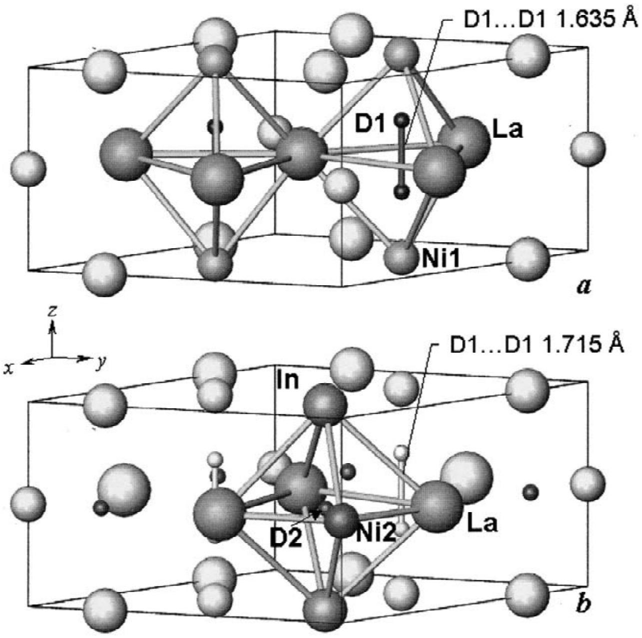

Fig. 3. The crystal structures of (a) $LaNiInD_{1.22}$ and (b) $LaNiInD_{1.63}$ deuterides showing occupied by deuterium atoms in trigonal bipyramid La_3Ni1_2 (D1) and octahedron La_3Ni2In_2 (D2).

In in the neighbourhood of D2 causes the very high displacement parameter for D2.

The most interesting feature of the structure of $LaNiInD_{1.63}$ deuteride is the occupation by D atoms of the interstices formed with participation of In. From the available crystal structure data for the ternary intermetallic hydrides of chemically related Al- and Ga-containing intermetallics, two other *p*-elements of the III group, it is known that H atoms enter Al-containing interstices Tb_3Al ($Tb_3Ni_6Al_2D_{6.8}$ [7]) and Tb_2NiAl ($TbNiAlD_{1.04}$ [8]) but do not form chemical bonds with Ga ($Nd_6Fe_{13}GaD_{12.3}$ [9]). The In–H interaction is different from the Al–H bonding. The H atoms enter Al-surrounded tetrahedral sites in the Al-containing intermetallic hydrides, whereas for $LaNiInD_{1.63}$ they are inserted into the large octahedral sites La_3Ni2In_2, $r \sim 0.63$ Å, rather than into the smaller tetrahedral interstices La_2Ni1In, $r \sim 0.40$ Å. The observed length of the hydrogen–indium bond (2.346 Å) is much longer than $r_{In} + 0.4 = 2.06$ Å. In the hydrogenated Al-containing intermetallics the Al–H distances (1.65–1.99 Å) are close to $r_{Al} + 0.4 = 1.83$ Å and also close to the value of Al–H distance observed in the AlH_3 trihydride, 1.715 Å [10].

The D . . . In bonding is weak. The deuterium desorption from $LaNiInD_{1.63}$ to form $LaNiInD_{1.22}$ [4] occurs already when the deuterium pressure is reduced below 1 bar (at room temperature) [1]. H is also rather weakly bonded to the La_3Ni sites, with H . . . H repulsion contributing to the development of the ‘loose’ bonding. This repulsion to form dihydrogen is not overcome even at pressures up to 40 GPa [11].

4. Conclusions

The present in situ study of the $LaNiInD_{1.63}$ deuteride shows that deuterium insertion into the $LaNiInD_{1.22}$ to form $LaNiInD_{1.63}$ is accompanied by very small modifications of the dimensions and anisotropy of the expansion of the unit cell. In the saturated deuteride $LaNiInD_{1.63}$ the D1 . . . D1 pair becomes ~6% longer compared to $LaNiInD_{1.22}$ (1.715 and 1.635 Å, respectively). The Ni . . . D bond remains rather nonaffected by the changes in D content with bond length (1.494 Å) close to the value characteristic for the covalent Ni . . . H bonding.

The crystal structure of $LaNiInD_{1.63}$ represents the first example of an intermetallic hydride where D atoms have In atoms in their surrounding. In addition to the nearly completely occupied La_3Ni sites, hydrogen atoms in $LaNiInD_{1.63}$ enter the deformed La_3NiIn_2 octahedra. The smaller La_2NiIn sites remain empty. This makes $LaNiInD_{1.63}$ different from the chemically related Al-containing ternary intermetallic hydrides.

There are no crystal chemistry limitations to reach 100% occupancy of the D2 La_3NiIn_2 sites. Therefore, the experimentally observed limit of the H storage capacity is related to the electronic structure rather than the crystal chemistry.

Acknowledgements

This work has received support from the Research Council of Norway.

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