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High pressure synchrotron XRD study of the pressure induced structural changes in LaNiInD$_{1.63-x}$

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Abstract

Unusual intermetallic deuteride LaNiInD$_{1.63-x}$ containing D . . . D pairs with very short D . . . D separations of 1.63 Å has been studied at 200 K at pressures up to 40 GPa by high-pressure synchrotron X-ray diffraction. In the elastic region ($<$20 GPa) the compression of LaNiInD$_{1.63-x}$ is close to isotropic; $\Delta a/a=-4.1\%$, $\Delta c/c=-4.3\%$, $\Delta V/V=-12.5\%$. At higher pressures ($20<P<40$ GPa) a hysteresis in the compressibility behaviour of a and c is developed. The application of high pressures results in a rather moderate reduction of the D . . . D separations (1.63 Å at 1.1 GPa vs. 1.47 Å at 39.5 GPa). The compressibility of the deuteride is dominated by the behaviour of the metal sublattice. Higher pressures are required to achieve further approach of H atoms to each other with a possible establishment of a H . . . H bonding interaction.

Keywords: Hydrogen storage materials; Crystal structure; High pressure; Diffraction; Synchrotron radiation

1. Introduction

Maximum H storage capacity of the metal hydrides depends on the structure of the hydrogen sublattice and is governed by the repulsive interactions between the hydrogen atoms. In typical hydrides, 2 Å is regarded as a limiting value for the H . . . H interatomic separations [1,2] yielding a H volume density of 294 g/l (close packed H sublattice) or, equivalently, 4.1 times higher compared to LH$_2$.

Recent studies have shown that much shorter D–D separations are observed in a new type of intermetallic hydrides, RNiInD$_{1.22}$ (R=La, Ce and Nd) [3] (RNiIn intermetallic compounds crystallise in the hexagonal ZrNiAl-type structure). Here a formation of a pair of deuterium atoms with D . . . D distance of around 1.6 Å takes place. This feature is unique among structurally characterized metal hydrides, consequently increasing practical limits of H volume content which can be reached in the metal hydrides. Formation of such H . . . H pairs can be compared with the compounds of dihydrogen, former containing H . . . H pairs at distances in the range from the value characteristic for the H$_2$ molecule (0.74 Å) to 1.4–1.5 Å [4], the experimentally observed higher limiting value of such distances for the bonded dihydrogen.

Application of high pressures to condensed hydrogen explores the possibilities to increase H volume content in the materials and is a subject of a vast number of both theoretical and experimental studies. Compressibility of solid H$_2$ has been studied in [5,6]. Modelling of H behaviour at super-high pressures was reported in a number of works (see, for example Ref. [7]). One major reason for such an interest is a possibility of achieving metallic hydrogen state where from a structural point of view *atomic* hydrogen forms a lattice with a very high volume density of H, approximately 16.9 times higher compared to LH$_2$ (diamond type structure, $d_{\mathrm{H-H}}=0.97$ Å). Furthermore, theory does not exclude a possibility that metallic hydrogen can exist in metastable state after releasing pressure to the ambient level, with obvious practical consequences.

Since estimated pressure range necessary to achieve metallic hydrogen state is very high, the other possible approach to synthesise metallic hydrogen is to use metal hydrides where H is already present in atomic form. Compression of metal hydrides can bring H atoms to a close approach thus forming a 'metallic' H sublattice. So

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far, the experimentally applied pressures in high-pressure studies of binary and ternary metal hydrides (<35 GPa) were below the necessary experimental limits. Such studies were performed for a number of binary hydrides with H...H distances exceeding 2 Å, e.g. ZrD_2 [8], VD_2 [9], SmD_2 [10], AlH_3 [11,12] and also intermetallic hydrides, e.g. YMn_2D_4 [13].

The present work was aimed at studies of the compressibility behaviour of the shortly separated D...D pair incorporated into the metal lattice. In addition, the system was searched for pressure induced phase transitions. High pressure studies at P up to ~40 GPa were performed for $LaNiInD_{1.63-x}$.

2. Experimental

A sample with equiatomic composition LaNiIn was prepared from a mixture of elemental lanthanum, nickel and indium (purity 99.9%), by arc melting in an argon atmosphere. It was annealed in an evacuated quartz tube at 600 °C for 4 weeks and thereafter quenched into ice water. The sample was deuterated at room temperature at a deuterium pressure of 6 bar (deuterium purity 99.8%). The synthesis gave a saturated deuteride $LaNiInD_{1.63\pm0.05}$, as indicated by in situ neutron powder diffraction study [14]. After reloading in the Ar glove box into the cell for the SR X-ray diffraction (XRD) study, the sample slightly released deuterium. This resulted in a two-phase material containing the higher deuteride $LaNiInD_{1.63-x}$ [$a=7.3756(1)$; $c=4.6697(1)$ Å] as the main constituent and the lower deuteride $LaNiInD_{0.67-x}$ [$a=7.610(3)$; $c=4.049(3)$ Å] as the minor admixtural phase.

High-pressure synchrotron powder XRD data were collected at beamline ID09 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Diffraction data were collected in the pressure range 1–40 GPa, both on compression and decompression, with a typical measurement step of 1–2 GPa. Pressure was measured by the $SrB_4O_7{:}Sm^{2+}$ fluorescence method [15]. The data were measured in two different compression–decompression experiments, with one experiment covering the pressure range up to 20 GPa and the other one extending this range to 40 GPa. In order to suppress hydrogen mobility and diffusion of the metal atoms, the experiments were carried out at 200 K. The experiments were performed in a membrane-type diamond anvil cell with the sample loaded into a hole in a stainless steel gasket with diameter of 130 μm and an initial thickness of 30 μm. The cells were placed into the cryostat. Nitrogen was used as the pressure-transmitting medium. It solidifies at 1 GPa at 200 K and, dependent of the applied pressure, several allotropic modifications are formed (see Ref. [16] and references therein). Reflections from solid N_2 are present in the diagrams collected at pressures higher than ~2 GPa. Unit-cell parameters of the lower deuteride were not refined owing to peak overlap with the reflections from solid N_2.

The powder X-ray diffraction data were collected on an image plate, scanned and thereafter integrated with the computer program Fit2D [17] before being transformed to a one-dimensional data set. The monochromator was a single reflection Si(111) monochromator with a wavelength of 0.417307 Å. The two-dimensional (2D) image plate distance and the wavelength were calibrated using Si in a separate experiment.

3. Results and discussion

In $LaNiInD_{1.2-1.6}$ the D–D pair at $d=1.63$ Å is aligned along c of the hexagonal ZrNiAl-structure (space group $P\bar{6}2m$) and belongs to the chain Ni–D–D–Ni ($c=2\,d_{\text{Ni-D}}+d_{\text{D-D}}$). Deuterium atoms fill with a double occupancy the trigonal bipyramid La_3Ni_2. Geometry of this bipyramid is mainly determined by the following interatomic distances: La–La (basal plane), Ni–D (along c) and D–D (along c) (Fig. 1). The values of these distances are affected by: (i) unit-cell parameters, a and c; (ii) sequence c/a; (iii) variables in the atomic coordinates of La [$x(3g)$] and D [$z(4h)$]. The latter parameters adopt the following values in $LaNiInD_{1.22}$ at 293 K and under normal pressure conditions: $x(3g)=0.6028(5)$; $z(4h)=0.676(1)$. Increase/decrease of $x(3g)$ from the reference value decreases/increases $d_{\text{La-La}}$. Decrease of $z(4h)$ from 0.676 decreases $d_{\text{D-D}}$ and increases $d_{\text{Ni-D}}$ with opposite effects following an increase of $z(4h)$. On application of pressure, the anticipated shrinking of the trigonal bipyramid can proceed in different ways, via isotropic contraction or anisotropically, with the main effect associated with the compression along c. The most dramatic effects on $d_{\text{D-D}}$ can be expected following a collapse of c/a from the value characteristic for $LaNiInD_{1.63-x}$ (0.629) to much smaller values observed for both lower deuteride $LaNiInD_{0.48}$ (0.529) and intermetallic compound LaNiIn (0.533).

Refinement of the starting SR XRD data set at the lowest pressure applied (1.1 GPa) showed that the sample under investigation contained the higher $LaNiInD_{1.63-x}$

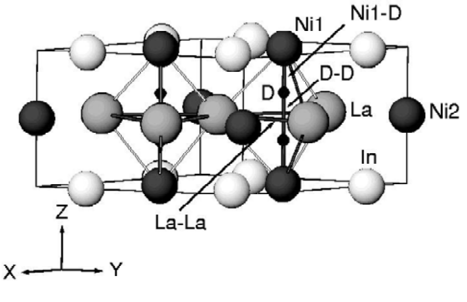

Fig. 1. The crystal structure of $LaNiInD_{1.63-x}$. Deuterium atoms fill with a double occupancy the trigonal bipyramid La_3Ni_2. Interatomic distances: La–La (basal plane), Ni–D (along c) and D–D (along c) are shown.

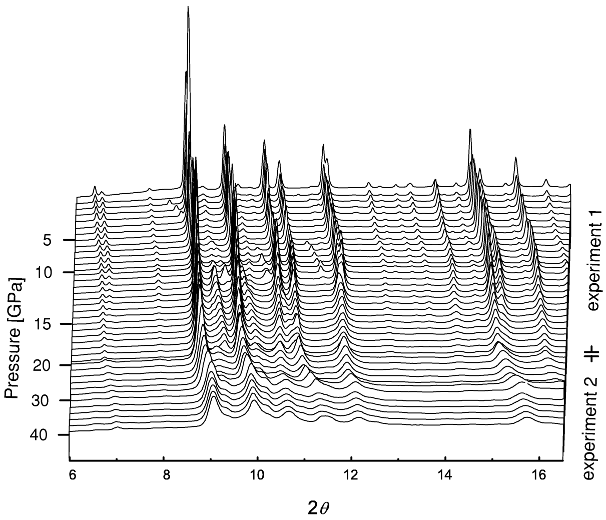

Fig. 2. Powder diffraction pattern of LaNiIn$D_{1.63-x}$ at pressures from 1.1 to 39.5 GPa ($T=200$ K).

deuteride as its major constituent (97.6 wt.%), with a small admixture of the lower deuteride LaNiIn$D_{0.67-x}$ (2.4 wt.%). The crystal structure data agree well with the reference data for LaNiIn-based deuterides [3].

Analysis of the pressure evolution of the diffraction data collected at pressures up to 40 GPa (see Fig. 2) showed that:

(i) Major details of the diffraction pattern remain unchanged indicating absence of structural phase transitions.
(ii) Peaks gradually shift towards higher angles, as a result of the contraction of the lattice.
(iii) The crystallinity of the sample decreases progressively at pressures above 20 GPa.
(iv) Extra diffraction peaks are observed, mainly originating from the crystallisation of the pressure medium, nitrogen and, also, from increased amount of the lower deuteride LaNiIn$D_{0.67-x}$ at pressures above ~14 GPa.

There are two distinctly different regions in the compressibility diagram:

(i) Elastic area (<~20 GPa) where a reversible compression–decompression takes place.
(ii) High-pressure area (>~20 GPa) where a pronounced hysteresis is observed.

The elastic region covering the range from 1.1 to 19.5 GPa is characterised by completely reversible transformations proceeding without a significant hysteresis on changing from loading pressure to its release. There are no significant differences in the compressibility along [001] and in the basal plane and no indication of a symmetry lowering of the metal sublattices in LaNiIn$D_{1.63-x}$ in this pressure range. The compression of LaNiIn$D_{1.63-x}$ is close to isotropic; $\Delta a/a=-4.1\%$, $\Delta c/c=-4.3\%$ and $\Delta V/V=-12.5\%$ (1.1 to 19.5 GPa). The crystallinity of the sample does not change on pressure up–down cycle. The quality of the Rietveld fits is fairly good in this pressure range (see Fig. 3 with two typical examples of the diffraction pattern).

Unit-cell dimensions of LaNiIn$D_{1.63-x}$ from the Rietveld refinements in GSAS of all data sets in the pressure range 1.1 to 19.5 GPa are given in Fig. 4. Because of progressive decrease in the crystallinity of the sample in the high-pressure area, the data from this pressure range was suitable only for the refinements of unit-cell parameters (shown in Fig. 4 as dotted lines). The crystallinity was deteriorated further with time, on a 'pressure down' dependence (after application of the highest pressure ~40 GPa). Another possible reason for the increased line widths at high pressures could be pressure inhomogeneities inside the cell.

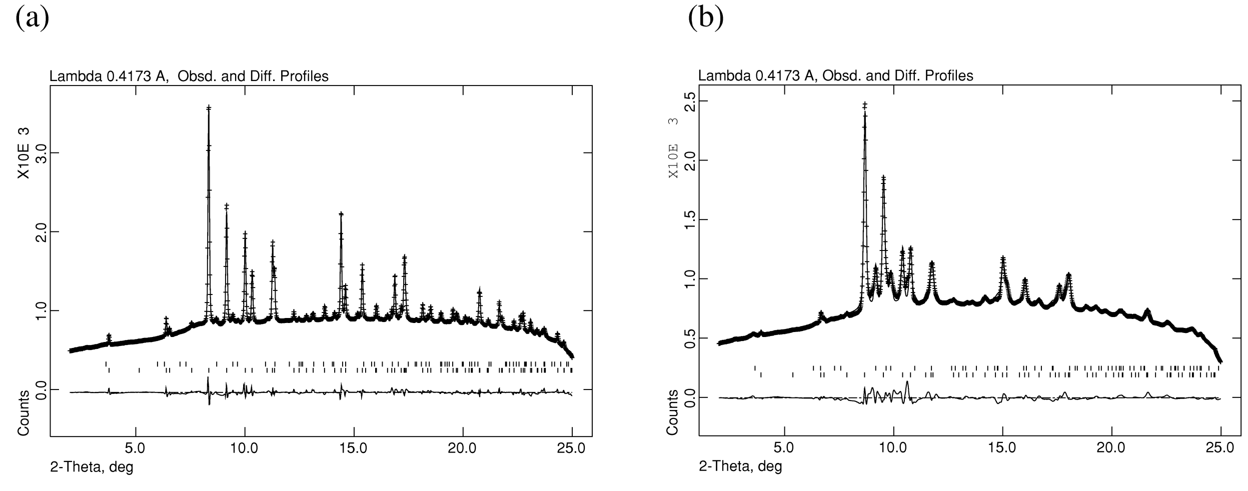

Fig. 3. Observed (+), calculated (upper line) and difference (lower line) XRD diffraction profiles for LaNiIn$D_{1.63-x}$. Positions of the peaks for the constituent phases are marked (from bottom to top): LaNiIn$D_{1.63-x}$ and LaNiIn$D_{0.67-y}$ at (a) 1.1 GPa and (b) 17.4 GPa.

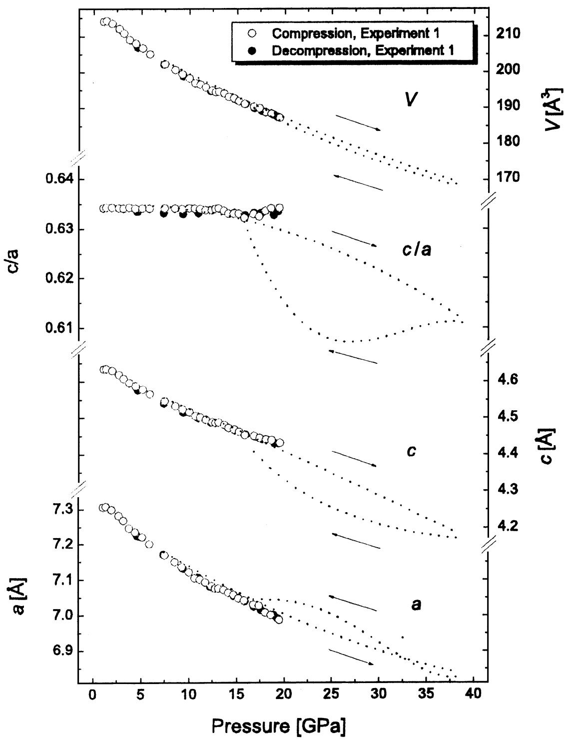

Fig. 4. Pressure dependence of the unit-cell dimensions and their ratio c/a (200 K) of the hexagonal $LaNiInD_{1.63-x}$ in the elastic region (1.1–19.5 GPa, experiment 1) and in the 'high pressure' area, 20–39.5 GPa (dotted lines, experiment 2).

Volume contraction $\Delta V/V$ for $LaNiInD_{1.63-x}$ is $\sim -21\%$ following pressure increase from 1.1 to 39.5 GPa. The pressure–volume data set ($P<20$ GPa; estimated zero volume $V_0 = 216.28$ Å^3) was fitted to a Birch–Murnaghan equation of state [18] yielding the resulting bulk modulus B and its pressure derivative B_0 of, respectively, 96(3) GPa and 4.8(5) GPa.

On transition to a higher-pressure range ($>\sim$20 GPa), the lattice becomes more compressible along c which is manifested by a change in the slope of the pressure dependence of $\Delta c/c$. In contrast, no significant changes in compressibility of a is observed in the range 20–40 GPa. On decompression the lattice retained in the 'compressed' state along [001], but quickly relaxed in the basal plane. This is also clearly visible in the modulations of the c/a ratio which above 20 GPa significantly decreases from the nearly constant value of 0.634 for $P<20$ GPa and, furthermore, exhibits a strong hysteresis on the pressure up–down cycle. At 20 GPa the size of the hysteresis of a is 1% and c is -1.7%. However, the pressure-induced effects on a and c compensate each other, so the volume dependence on compression/decompression is very similar, with a very small hysteresis effect only. Since the unit-cell dimensions return to original values on decompression, hydrogen content in the higher deuteride $LaNiInD_{1.63-x}$ is expected to be constant at pressures up to 40 GPa. Nevertheless, some amount of $LaNiInD_{1.63-x}$ decomposes thus increasing the content of lower deuteride $LaNiInD_{0.67-x}$.

From the data presented in Table 1 it is evident that application of high pressures does not induce any significant deformation of the metal sublattice. The refined values of parameter x both for La ($3f$) and In ($3g$) remain practically unchanged. Assuming that the positions of the D atoms do not change with pressure, the values of the metal–deuterium and deuterium–deuterium distances were estimated (see Table 1), the latter reaching 1.469 Å at the highest pressure applied. This shows that no collapse of the H . . . H separation is induced in the studied pressure range, thus indicating nonbonding H–H interactions.

It is interesting to compare the results obtained with the reference compressibility data for solid deuterium [5] and with the high-pressure studies of the metal hydrides [8–

Table 1
Unit-cell dimensions, atomic coordinates and interatomic distances in $LaNiInD_{1.63-x}$ at ambient pressure (298 K) and at pressures 1.1, 17.4 and 39.5 GPa[a] (200 K)

		Ambient pressure (298 K)	1.1 GPa	17.4 GPa (200 K)	39.5 GPa[a]
Structure type of the metal sublattice			ZrNiAl		
Space group			$P\bar{6}2m$ (No. 189)		
Unit-cell dimensions (Å)	a	7.3755(1)	7.3053(2)	7.0264(6)	6.830(1)
	c	4.6697(1)	4.6325(1)	4.4442(5)	4.174(2)
Atoms and their coordinates	La in $3g$; x	0.6028(5)	0.604(1)	0.603(1)	*0.603*
	In in $3f$; x	0.2427(4)	0.245(1)	0.244(2)	*0.244*
Interatomic distances (Å)	La–La	4×3.915(2)	4×3.886(3)	4×3.729(6)	*4×3.626*
	La–Ni	4×3.250(1)	4×3.225(1)	4×3.094(2)	*4×2.956*
	La–D[b]	4×2.405(1)	4×2.387(2)	4×2.291(3)	*4×2.219*
	Ni–D[b]	2×1.513(1)	2×1.501(1)	2×1.440(1)	*2×1.352*
	D–D[b]	*1.635*	*1.630*	*1.563*	*1.468*
Reliability factors	R_{wp}	0.0135	0.0189	0.0244	–
	R_p	0.0092	0.0129	0.0169	–

Calculated values are in italic. Sites: La in $3g$, x,0,1/2; Ni1 in $1b$, 0,0,1/2; Ni2 in $2c$, 1/3,2/3,0; In in $3f$, x,0,0; D in $4h$, 1/3,2/3,z.

[a] Interatomic distances estimated assuming the same atom positions as for 17.4 GPa.

[b] Calculated values. The D position was kept constrained at $z = 0.676(1)$ (298 K, 1 bar [3]).

12]. Molecular deuterium at pressures up to 30.9 GPa undergoes volume compression of 42.6% without metallization, i.e. significantly higher than the value 21% for $LaNiInD_{1.63-x}$ at pressures up to 39.5 GPa. In solid deuterium [5] the shortest possible D–D distance assuming rotational disorder of the D_2 molecules decreases from 1.89 Å at 6.17 GPa to 1.43 Å at 30.9 GPa (298 K, suggesting a noncompressibility of the deuterium molecule with $d_{D-D}=0.74$ Å). In binary hydrides with high H content (AlH_3 [12]) the compression mainly results in an H . . . H contraction between neighbouring AlH_6 coordination polyhedra leaving practically unchanged the Al–H distances and the geometry of these polyhedra. The studies [8–12] showed that binary hydrides can be less compressible (ZrD_2 [8]), more compressible (AlH_3 [11]) or can have nearly the same compressibility (VD_2 [10]) compared to related metals. However, in all cases including transition metals the compressibility of the metal hydrides does not differ significantly from the behaviours observed for the corresponding metals.

In conclusion, comparison of the results of this work with the available reference data shows that hydrogen–hydrogen repulsion can be overcome to a high extent by application of pressure and that the compression behaviour of the intermetallic hydride at low H content in the metal matrix is determined by the compressibility of the metal sublattice mainly. Such a conclusion is supported by theoretical calculations of the equations of state for LaNiIn and $LaNiInD_{1.63-x}$ [18].

Finally, this study shows that higher pressures are required to reach a larger contraction of the metal sublattice allowing H atoms to chemically interact with each other with a possible establishment of H–H bonds within the metallic cluster.

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