# SYNTHESIS AND CRYSTAL STRUCTURE OF OVER-STOICHIOMETRIC DEUTERIDE $LaNi_5D_{9.5}$

**Sakharov M.K.**[*], **Agafonov S.S.**[(1)], **Antonov V.E., FedotovV.K., Sagoyan L.I.**
Insitute of Solid State Physics RAS, 142432 Chernogolovka, Moscow district, Russia
[(1)] Russian National Centre "Kurchatov Institute", Kurchatov sq. 1, 123333 Moscow, Russia
[*]*Fax: +7(496) 524 9701* *E-mail: sakharov@issp.ac.ru*

## Introduction

The $LaNi_5H_x$ hydride with $x \leq 6$ has been widely used as hydrogen storage material for many decades. Long ago, in 1973 [1], it was also predicted that the hydrogen content of this hydride could be increased to $x > 6$ by applying high hydrogen pressure. A few years later [2], $LaNi_5$ was in fact found to absorb $x \approx 8$ of hydrogen at a pressure of 1.4 kbar and room temperature. This hydrogen content corresponded to the composition of a $LaH_3$ + 5NiH mixture of binary hydrides, which were thermodynamically stable under the synthesis conditions. Neither the crystal structure, nor phase composition of the samples were examined in [2].

The present paper reports on the high-pressure synthesis of a new $LaNi_5H_x$ hydride with $x \approx 9.5$. This composition can be regarded as "over-stoichiometric", because no intermetallic compound of a rare-earth metal (R) and a group VI–VIII transition metal (M) has ever formed hydride containing more hydrogen than a mixture of $RH_3$ and MH. We prepared both hydride $LaNi_5H_{9.5}$ and deuteride $LaNi_5D_{9.5}$ and studied their thermal stability in vacuum and examined the crystal structure of $LaNi_5D_{9.5}$ by X-ray and neutron diffraction.

## Results and discussions

Powder samples of $LaNi_5H_{9.5}$ and $LaNi_5D_{9.5}$ weighing 0.8 g each were collected of batches about 50 mg each prepared by exposing $LaNi_5$ to a hydrogen/deuterium pressure of 90 kbar and a temperature of 100 or 300°C for 48 h. After the hydrogenation was completed, the batch was quenched to –170°C to prevent its decomposition while releasing the pressure. A portion of a few milligrams of every batch was analysed for hydrogen or deuterium content by hot extraction in vacuum (Fig. 1). The batches with the total hydrogen content of $x = 9.5 \pm 0.4$ were only used to compose the $LaNi_5H_{9.5}$ and $LaNi_5D_{9.5}$ samples.

As seen from Fig. 1, gas evolution from the batches started at –100 to –70°C and the desorption curves showed a plateau of $\Delta x = 0.3$–0.4 near room temperature. The evolution of $x \sim 6$ of the residual gas on further heating depended on the synthesis temperature of the sample and was different for the two hydrogen isotopes used.

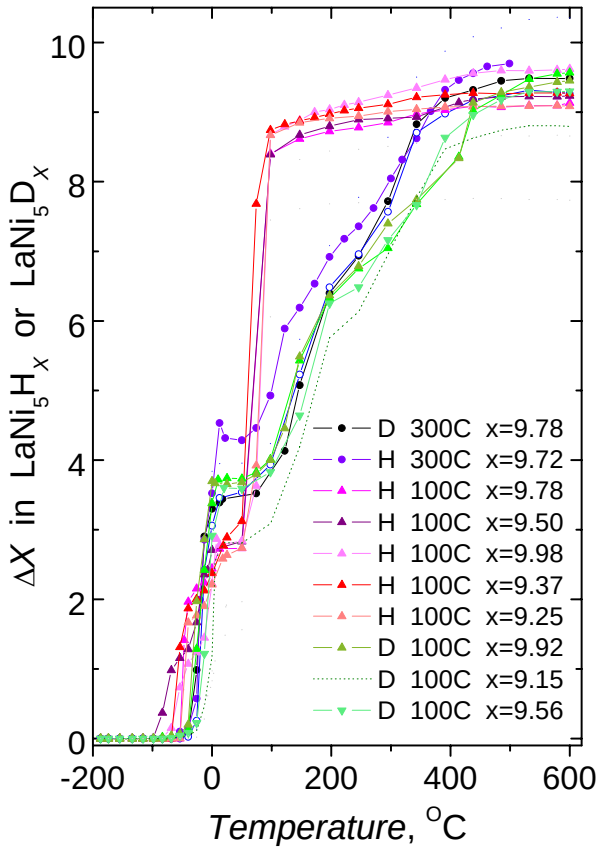


Fig. 1. Hydrogen/deuterium desorption from $LaNi_5H_x$ and $LaNi_5D_x$ batches in the course of heating in a pre-evacuated volume at a rate of about 20°C/min.

The X-ray investigation of the quenched $LaNi_5D_{9.5}$ sample was carried out at 90 K using a Siemens D500 diffractometer equipped with a nitrogen cryostat that allowed the loading of powder samples without their warming above the liquid $N_2$ temperature. The obtained X-ray pattern (Fig. 2) can be modelled, in a first approximation, by mixture of two crystalline phases, $LaNi_2D_x$ + $3NiD_y$. Structural parameters of these phases are shown in the Fig. 1.

Hydrogenolysis is typical of many intermetallic compounds. The two-phase model could provide for the mean deuterium content $x = 9.5$ of the sample assuming $x \approx 7$ and $y \approx 1$. Both

compositions are admissible from the viewpoint of crystal chemistry.

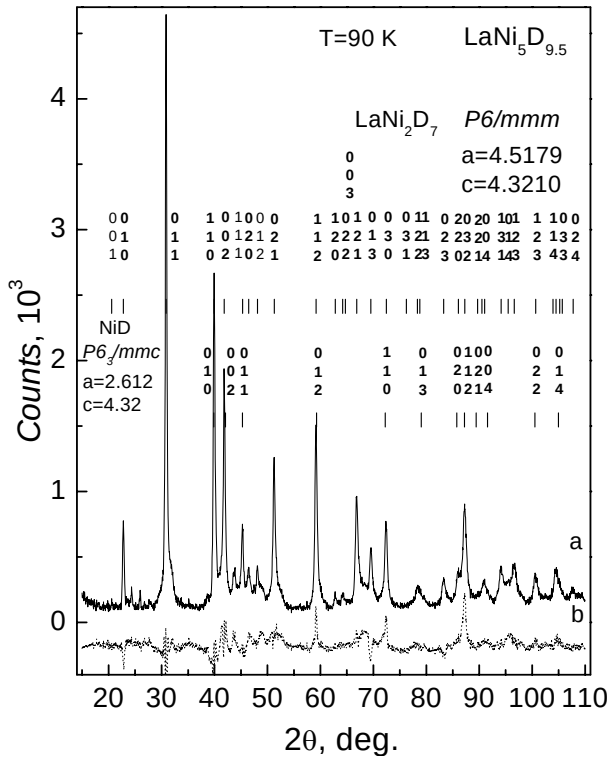


Fig. 2. X-ray diffraction pattern of the $LaNi_5D_{9.5}$ sample synthesized under a $D_2$ pressure of 90 kbar and $T$ = 300°C and measured at ambient pressure and 90 K using Cu $K_\alpha$ radiation (solid curve). The dotted curve shows the difference spectrum resulting from modelling the experimental pattern with a mixture of hexagonal phases $LaNi_2D_7$ + 3NiD.

X-ray diffraction is insensitive to positions of H or D atoms in the metal lattice. The crystal structure of $LaNi_5D_{9.5}$ was therefore examined by neutron diffraction using the DISK diffractometer at Kurchatov Institute.

As the first step to analyze the obtained neutron diffraction pattern (Fig. 3), we checked for the applicability of the two-phase model that semi-quantitatively explained the X-ray pattern of $LaNi_5D_{9.5}$ (Fig. 2).

Taking into account the limitations imposed by crystal chemistry, deuterium atoms could only occupy octahedral interstitial sites in the metal lattice of $NiD_x$ and two sorts of interstitial sites (4h and 6k) in $LaNi_2D_x$. The model with the octahedral co-ordination of D atoms in NiD (curve b in Fig. 3) did not contradict the experimental spectrum. At the same time, any arrangement of D atoms on the allowed interstitials in $LaNi_2D_x$ was inconsistent with experiment.

It is worth noting in this connection that the parameters of the proposed $LaNi_2D_7$ and NiD unit cells are linked by the relations $A \approx a\sqrt{3}$ и $C \approx c$. This suggests that $LaNi_5D_{9.5}$ sample could be single-phase and had a more complex crystal structure with the unit cell composed of structural units of the $LaNi_2D_7$ and NiD type.

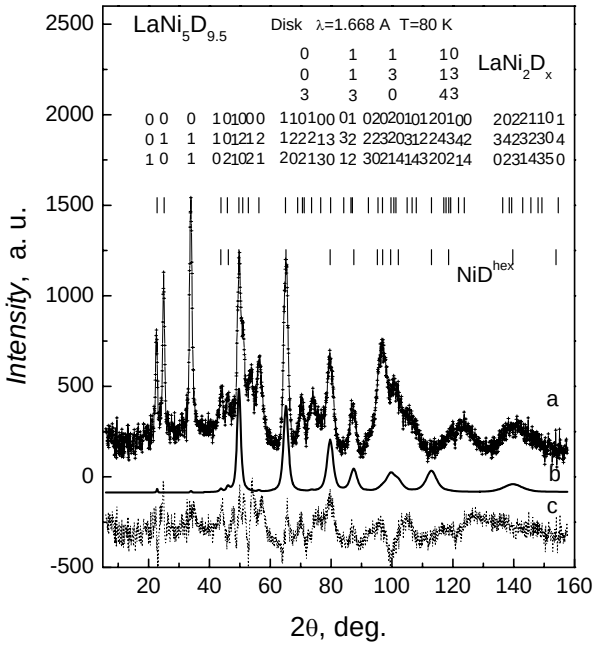


Fig. 3. Neutron diffraction pattern of the $LaNi_5D_{9.5}$ sample (a); the calculated contribution of NiD (b) and an example of the difference pattern (c) produced while modelling the experimental pattern with a structure combining fragments of $LaNi_2D_7$ and NiD unit cells.

**Conclusions**

New, over-stoichiometric deuteride $LaNi_5D_{9.5}$ is synthesized under high pressure and the basic motive of its complex crystal structure is revealed by X-ray and neutron diffraction studies.

**References**


1. Anderson JL, Wallace TG, Bowman AL, Radosevich CL, and Courtney ML. Hydrogen absoption by $AB_5$ compounds. Los Alamos Scientific Laboratory, Los Alamos, New Mexico, LA-5320, 1973.

2. Lakner JF, Uribe FS and Steward SA. Hydrogen and deuterium sorption by selected rare earth intermetallic compounds at pressures up to 1500 atm. J. Less-Common Metals, 72, 1980, p.87-105