Experimental report

23/09/2024

Proposal: 5-24-720 **Council:** 4/2023

Title: In situ investigations of the hydrogenation of Ni3In

Research area: Chemistry

This proposal is a new proposal

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Samples: Ni3Ga
Ni3In

Instrument	Requested days	Allocated days	From	To
D20	3	3	24/11/2023	27/11/2023

Abstract:

In situ neutron powder diffraction will reveal the hydrogen (deuterium) positions and occupations in the hydrides Ni3InHx(D)x (hexagonal filled Mg3Cd type) and the intermediate cubic Ni3InHz (filled AuCu3 type). The diffraction experiment will be performed in a user-supplied sapphire single crystal cell at deuterium pressures up to 70 bar and temperatures up to 750 K. Rietveld analysis of diffraction data will allow the location of deuterium positions in the deuterides and the mapping of the complete reaction pathway of deuterium uptake and release.

In situ investigations of the hydrogenation of Ni_3In (5-24-720)

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A variety of nickel-rich intermetallic compounds MNi_3 compounds are reported in the literature, *e. g.* for *M* = Mg, Al, Ga, Ge, Mn, Fe ($AuCu_3$ type), Zr, In, Sn (Ni_3Sn type), Hf ($BaPb_3$ type), V, Nb, Ta ($TiAl_3$ type), Nb, Mo, Sb (Cu_3Ti type), Ti ($TiNi_3$ type), lanthanides *Ln* ($CeNi_3$ type, $PuNi_3$ type). Except for nickel-rich lanthanide compounds, which are well-studied for their ability to form hydrides in distorted variants of the hydrogen-free parent intermetallic structures [1], nickel-containing hydrides with p-block or transition metals are less well known.

Ni_3In (Ni_3Sn structure type) was studied *in situ* by neutron powder diffraction data under deuterium pressure (D20 in high-resolution mode at λ = 1.87 Å, 2 min per pattern, sapphire single-crystal cell [2–5]) according to the following temperature-pressure protocol (**Figure 1**):

1) 7.7 MPa D_2: 300 K → 680 K → 300 K
2) 2.7 MPa D_2: 300 K → 700 K → 300 K
3) 0.9 MPa D_2: 300 K → 800 K → 300 K

The deuteration reaction of Ni_3In starts at around 395 K with the formation of α-Ni_3InD_x, leading to a significant increase in the *c* lattice parameter and a unit cell volume expansion of around 2.1%. Possible deuterium sites are [Ni_6] octahedral voids. The deuterium positions were established by alternating refinement of deuterium positions or occupation, followed by Fourier analysis. The α-Ni_3InD_x crystallizing in the hexagonal-filled Ni_3Sn structure type and deuterium was found to occupy the [Ni_6] octahedral voids (**Figure 2**, **Table 1**).

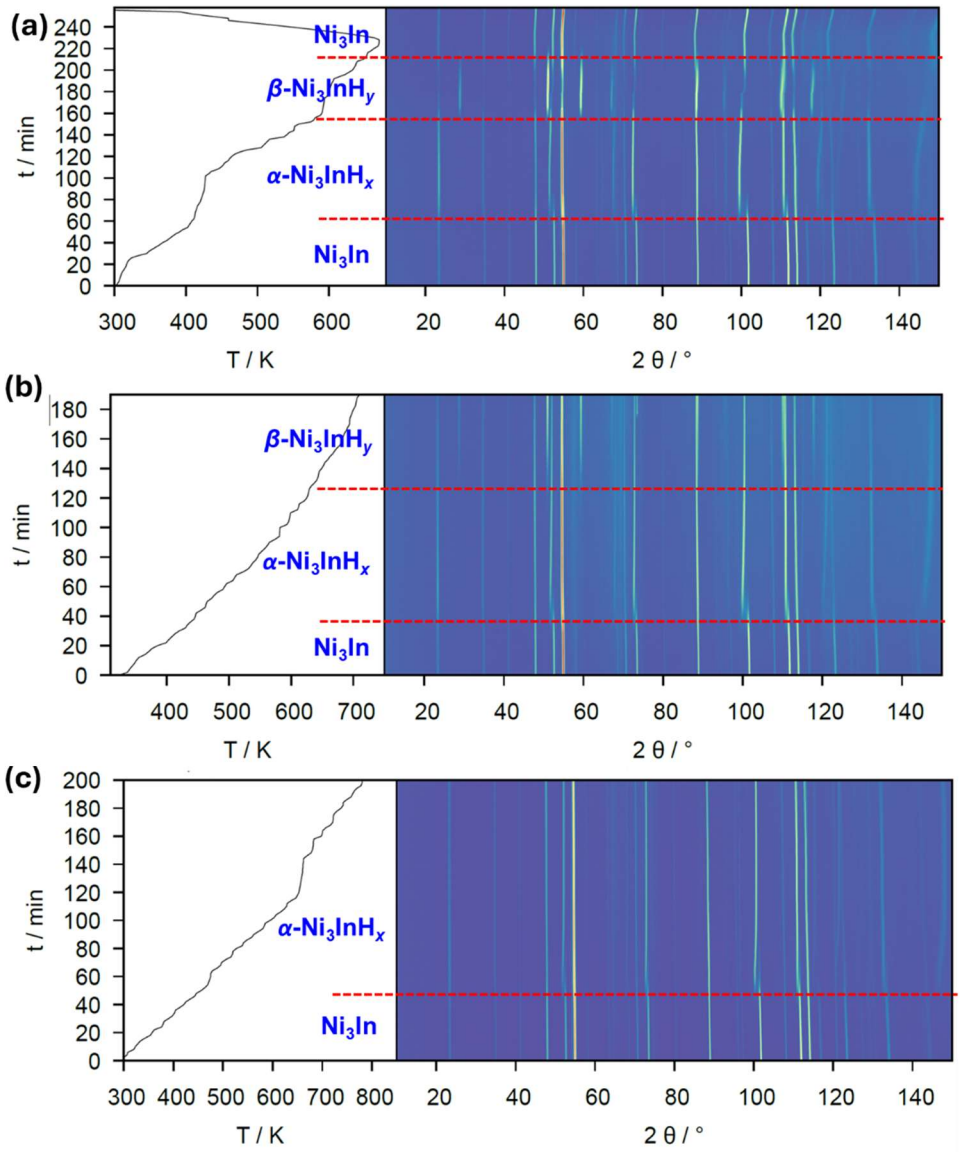

Figure 1: *In situ neutron powder diffraction data of the deuteration of Ni_3In taken on diffractometer D20 at λ = 1.86897(6) Å in a single crystal sapphire cell under various deuterium pressures and temperature conditions:* ***(a)*** *7.7 MPa D_2;* ***(b)*** *2.3 MPa D_2;* ***(c)*** *0.9 MPa D_2. Intensities are in false colors.*

Table 1: Refined atomic parameters of α-$Ni_3InD_{0.65(3)}$ ($P6_3/mmc$, a = 5.3427(9) Å, c = 4.3332(8) Å).

atom	Wyck.	*x*	*y*	*z*	*B* / 10^4 pm^2	Occ.
In1	2*d*	1/3	2/3	3/4	1.534(6)	1
Ni1	6*h*	0.1624(2)	0.3249(2)	1/4	1.424(8)	1
D	2*a*	0	0	0	2.589(3)	0.65(3)

Table 2: Refined atomic parameters of β-$Ni_3InD_{0.81(5)}$ ($Pm\bar{3}m$ = 3.7838(5) Å).

atom	Wyck.	*x*	*y*	*z*	*B* / 10^4 pm^2	Occ.
In1	1*a*	0	0	0	1.818(8)	1
Ni1	3*c*	1/2	1/2	0	1.454(4)	1
D	1*b*	1/2	1/2	1/2	2.485(3)	0.81(5)

Throughout heating the development of the α-Ni_3InD_x corresponds to a reduction of the Ni_3In phase fraction until around 425 K, where we exclusively observe the formation of the α-$Ni_3InD_{0.65(3)}$. The phase fraction of the hexagonal α-Ni_3InD_x phase remains constant until 550 K, when a new deuterated phase, β-Ni_3InD_y forms (filled $AuCu_3$ type, $Pm\bar{3}m$ a = 3.78431(4) Å, **Figure 3**, **Table 2**).

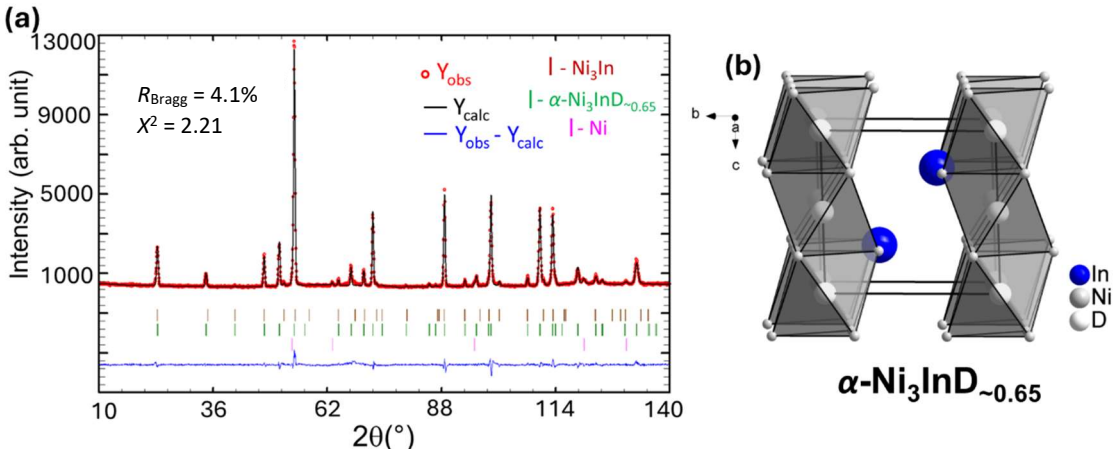

Figure 2: (a) Rietveld refinement and **(b)** crystal structure of α-$Ni_3InD_{0.65(3)}$ (D20, ILL, Grenoble, $\lambda_{neutrons}$ = 1.8689(2) Å, 7.7 MPa deuterium gas pressure, T = 422 K)

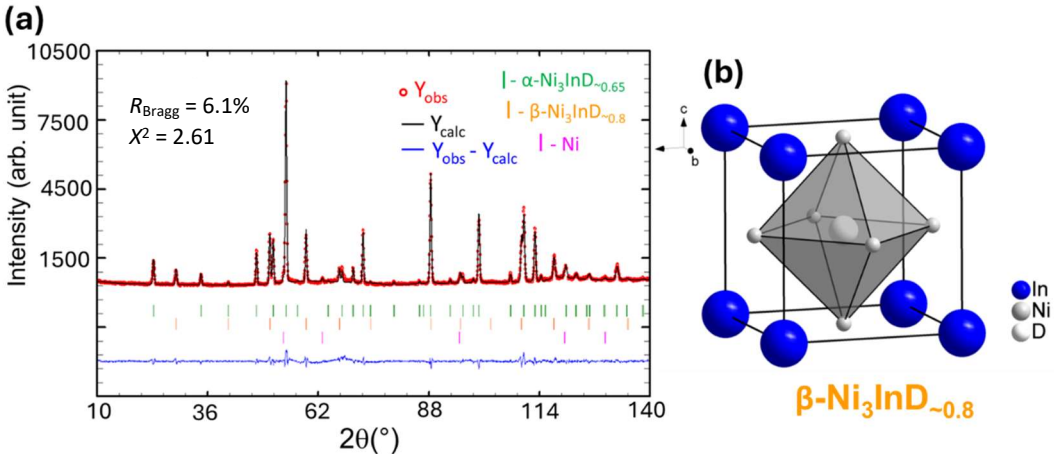

Figure 3: (a) Rietveld refinement and **(b)** crystal structure of β-$Ni_3InD_{0.8(5)}$ (D20, ILL, Grenoble, $\lambda_{neutrons}$ = 1.8689(2) Å, 7.7 MPa deuterium gas pressure, T = 581 K)

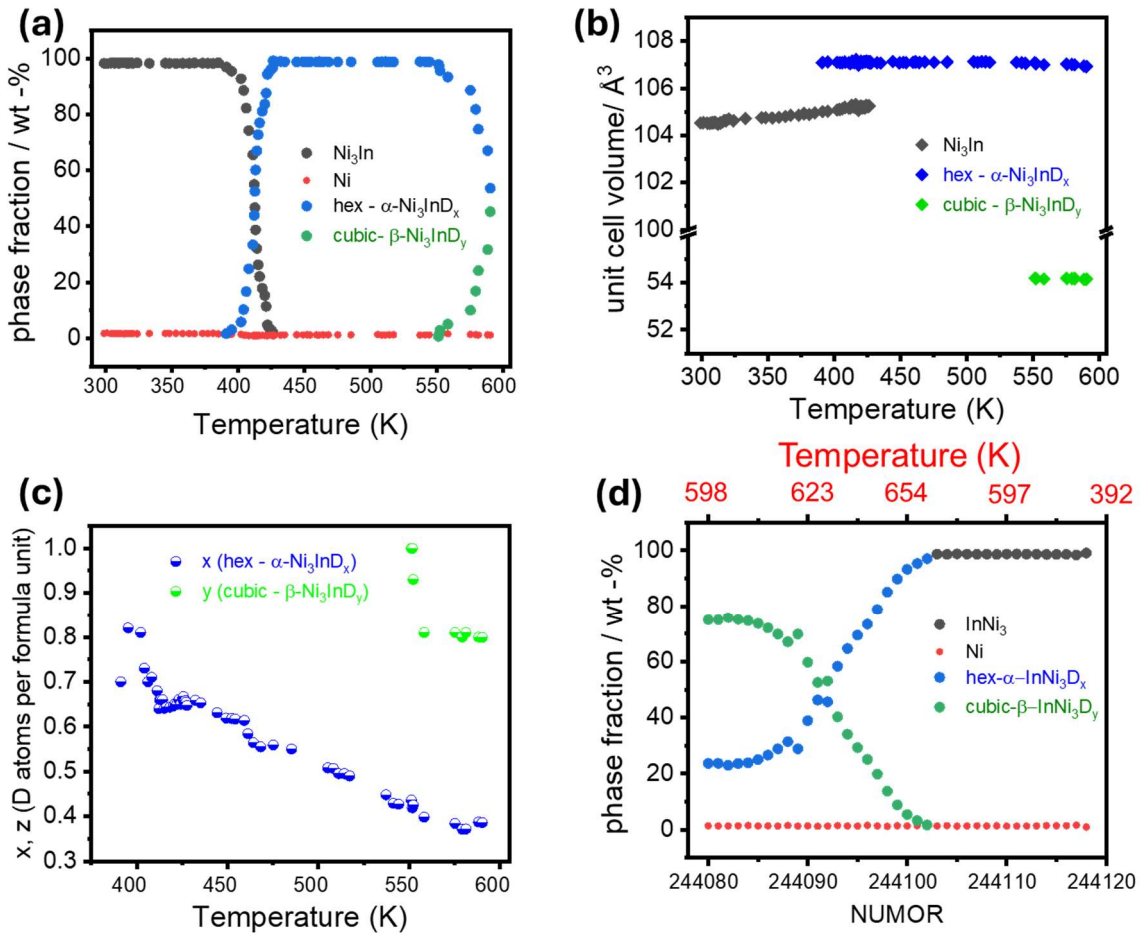

Figure 4: Control parameters of the *in situ* deuteration of Ni_3In and refined structural parameters based on neutron powder diffraction data measured at D20 (λ = 1.86897(6) Å) at 7.7 MPa D_2 and various temperatures: **(a)** phase fractions – upon heating, **(b)** unit cell volume – upon heating, **(c)** deuterium content per formula unit – upon heating, **(d)** phase fractions – upon cooling under vacuum. Each NUMOR 2 min.

At 550 K ≤ *T* ≤ 590 K, a miscibility gap between *α* - and *β* -phase is presumed, as both phases are observed simultaneously, and *α*-Ni_3InD_x has a sharp decrease of ≈ 0.44 deuterium atoms per formula unit. At around 590 K, we detected a reduction in deuterium pressure, suggesting a potential leak in the cell. Therefore, we decided to apply vacuum, heat the cell to 670 K and cool it down to room temperature. Upon cooling under vacuum, both hydrides decomposed around 665 K and the parent compound hexagonal Ni_3In formed (**Figure 4**).

References:

[1] Y. E. Filinchuk, K. Yvon, *J. Alloys Compd.* **2005**, *404-406*, 89-94.

[2] R. Finger, N. Kurtzemann, T. C. Hansen, H. Kohlmann, Design and use of a sapphire single-crystal gas-pressure cell for in situ neutron powder diffraction, *J. Appl. Crystallogr.* **2021**, *54*, 839–846.

[3] A. Götze, J. Möllmer, H. Kohlmann, *Inorg. Chem.* **2018**, 57, 10925−10934.

[4] A. Götze, H. Auer, R. Finger, T. C. Hansen, H. Kohlmann, A sapphire single-crystal cell for *in situ* neutron powder diffraction of solid-gas reactions, *Phys. B (Amsterdam, Neth.)* **2018**, *551*, 395–400.

[5] A. Götze, S. C. Stevenson, T. C. Hansen, H. Kohlmann, *Crystals* **2022**, 12,1704.