Structure and hydrogenation study of nickel substituted NdCo$_3$NiB

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ARTICLE INFO

ABSTRACT

In an attempt to observe hydrogen (deuterium) induced atomic ordering of transition (T) metals in AB$_5$-type derivative structures neutron diffraction and hydrogen cycling experiments were performed on a nickel substituted boride sample of composition NdCo$_3$NiB. While uncycled NdCo$_3$NiB crystallizes with the centrosymmetric CeCo$_4$B-type structure (space group $P6/mmm$), hydrogenation (deuteration) and cycling of NdCo$_3$NiB at 373 K between 0 and 60 bar hydrogen (deuterium) atmosphere induces a symmetry decrease to non-centrosymmetric space group $P6mm$. Evidence for partial cobalt/nickel ordering is found in pristine NdCo$_3$NiB but not in its deuteride NdCo$_3$NiBD$_x$. Compared to boron free AB$_5$-type compounds deuterium occupies only those interstices that have no boron atom in their coordination sphere. These findings are consistent with repulsive B–D interactions. At 303 K the hydrogen equilibrium plateau pressure of the NdCo$_3$NiB–H system is about 2 bar, and the hydrogen content at 10 bar is about 3.1 H atoms per formula unit.

1. Introduction

Ternary borides of composition RET_4B (RE = rare earth, T = transition metal) are potential hydrogen storage materials. They crystallize with the hexagonal CeCo$_4$B-type structure which derives from the well-known RET_5 hydrogen storage materials by an ordered substitution by boron on one of the transition metal sites. In the past, mainly cobalt and nickel based members have been studied. LaNi$_4$B, for example, was found to absorb 1.5 hydrogen atoms at room temperature (273–326 K) in the pressure range 0–100 atm, but its structure was not fully characterized [1]. Hydrogen absorption and desorption properties of RECo$_4$B (RE = La, Pr, Sm) and RENi$_4$B (RE = Ca, La, Pr) were also investigated [2]. The cobalt members absorbed about 4.5 hydrogen atoms per formula unit (f.u.) in the pressure range 0–100 atm, at 273–326 K. For some members hydrogen site occupancies were proposed [2] but not experimentally verified. Some compounds of this family were obtained *via* the chemical route and contained more than 4 hydrogen atoms per formula unit [3]. However, their hydrogenation properties and hydrogen distributions have not yet been measured. Among the hydrogen free compounds the hexagonal structure of NdCo$_4$B has been refined [4], while an orthorhombic distortion (space group *Imma*) has been reported for NdNi$_4$B [5].

Mixed T-metal boride systems belonging to this class have also been studied with respect to hydrogen storage properties, such as YCo$_3$NiB [6], SmCo$_3$NiB [7], [8] and PrCo$_3$NiB [9] but the structures were not fully characterized. Generally, the T-metals in such solid solutions are expected to be disordered. In fact, transition metal compounds displaying ordered arrangements of different transition metals are extremely rare. In the presence of hydrogen, however, such compounds may show an increased tendency of T-metal ordering. In fact, recent work on metal hydrogen systems suggested the presence of preferred T-metal hydrogen configurations as a function of the valency of the T-metal [10], in particular in the so-called complex d-metal hydrides [11,12]. The possibility of achieving hydrogen induced T-metal ordering, for example by cycling under hydrogen, would be of considerable practical and fundamental interest, but has not yet been investigated. Another interesting aspect of these compounds is the influence of boron on the D atom distribution. From previous work on other T-metal systems containing "light p-block elements" [13] such as B [14], C [15], Si [16], repulsive interactions are expected.

This paper reports on structural and hydrogenation properties of the mixed Co/Ni system NdCo$_{4-x}$Ni$_x$B–H in both uncycled and cycled states. The composition NdCo$_3$NiB was used for a detailed study because the tendency for T-metal ordering should be most pronounced at the compositional ratio Co/Ni = 3 as indicated by the multiplicities of the two transition metal sites in the CeCo$_4$B-type structure (6i and 2c in space group $P6/mmm$). Since boron substitutes for T-metals bonded to hydrogen in the B-free prototypes RET_5 its influence on the hydrogen distributions in the boride can be

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Table 1
Refinement results for the (a) uncycled (top) and cycled (bottom) NdCo$_3$NiB at room temperature from neutron powder diffraction.

Atoms	Site	x	y	z	B (Å^2)	Occ.
NdCo$_3$NiB (uncycled)						
Nd1	1a	0	0	0	1.23(6)	1.0
Nd2	1b	0	0	½	0.68(4)	1.0
T1	2c	1/3	2/3	0	1.48(7)	0.65(1) + 0.35(1)
T2	6i	½	0	0.2903(3)	0.69(3)	0.78(1) + 0.22(1)
^{11}B	2d	1/3	2/3	½	0.25(3)	1.0
NdCo$_3$NiB (cycled)						
Nd1	1a	0	0	0	1.17(6)	1.0
Nd2	1b	0	0	½	0.61(4)	1.0
T1	2c	1/3	2/3	0	1.56(8)	0.65(1) + 0.35(1)
T2	6i	½	0	0.2905(3)	0.66(3)	0.78(1) + 0.22(1)
^{11}B	2d	1/3	2/3	½	−0.04(3)	1.0
T = Co + Ni						

Space group $P6/mmm$ (N°191); $Z = 2$, $T = Co+$Ni; occupancy factors of cobalt and nickel on same site constrained to 1.0; isotropic Atomic Displacement Parameters (ADPs) of cobalt and nickel on same site constrained to be equal; no constraints on ADPs of T1 and T2. Uncycled NdCo$_3$NiB: $a = 5.0934(2)$Å, $c = 6.9163(3)$Å, $V = 155.39(1)$Å^3, $R_{Bragg} = 6.85\%$, $R_{wp} = 12.9\%$, $\chi^2 = 5.79$.
Cycled NdCo$_3$NiB: $a = 5.0931(1)$Å, $c = 6.9143(3)$Å, $V = 155.33(1)$Å^3, $R_{Bragg} = 9.54\%$, $R_{wp} = 7.61\%$, $\chi^2 = 7.15$.

conveniently studied and compared with that of the B-free proto-type. The structural studies were performed on deuterides by using neutron powder diffraction, and the hydrogen absorption char-acteristics were investigated by measuring pressure-composition isotherms (PCIs).

2. Experimental

Intermetallic compounds of nominal compositions NdCo$_3$NiB and NdCo$_4$B were prepared by arc melting compressed pellets of neodymium (pieces, purity: 99.9%) and cobalt, nickel and isotope enriched boron ^{11}B (powders, purity: 99.9%). Each sample was melted three times while turning over the ingots. The weight loss of each ingot after melting was less than 0.2 wt%. The ingots were sealed into quartz tubes under 250 mbar of Argon, annealed for one week at 1073 K and then quenched in cold water. No reaction occurred between the ingots and the walls of the quartz tubes. X-ray powder diffraction (OMNI, λ_{Co}) showed that the samples were single-phase and consisted of the expected hexagonal phases. The samples were then deuterated at 373 K under 60 bar of D$_2$ (99.8%, AGA) for one week in high-pressure stainless steel autoclaves without preliminary activation. Before opening the autoclaves, the latter were slowly cooled down to room tem-perature. For NdCo$_3$NiB three absorption–desorption cycles were carried out to examine a possible onset of hydrogen-induced metal atom ordering. The exper-iments were conducted as follows: first, the sample (6 g) was evacuated under vacuum (4.10^{-2} mbar) at 373 K during one hour; then the autoclave was charged with 60 bar of D$_2$ at $T = 373$ K and left under these conditions for 4 days; the pres-sure was then slowly released and the autoclave evacuated under dynamic vacuum (4.10^{-2} mbar) for around 12 h ($T = 373$ K). This treatment was repeated twice, lead-ing to three absorption–desorption cycles. During the last desorption, the sample was evacuated under dynamic vacuum for two days, in order to achieve complete desorption.

Neutron diffraction patterns were collected on both cycled and uncycled inter-metallic NdCo$_3$NiB and their deuterides NdCo$_3$NiBD$_x$ on the high-resolution powder diffractometer HRPT at SINQ (Paul Scherrer Institute, Villigen, Switzerland) in the high-intensity mode: $\lambda = 1.1545$Å, $2\theta = 5$–165°, step size $2\theta = 0.1$°, data collec-tion time around 10 h; ex situ measurements of uncycled samples: double-walled vanadium cylinders, $T = 298$ K; in situ measurements of cycled samples: cylindrical stainless steel container placed into a furnace and connected to a deuterium pressure line, $T = 373$ K, D-pressure = 10–15 bar. All diffraction profile and structure refine-ments were carried out by using the FullProf Suite software [17]. For the cycled deuteride sample diffraction peaks from the face centered cubic stainless steel con-tainer were modeled using full-pattern matching implemented in that software.

Pressure-Composition Isotherms were measured on activated NdCo$_3$NiB and NdCo$_4$B on a fully automated Sievert's-type volumetric instrument (PCTPro 2000, Hy-energy LLC, Fremont (CA), USA). Samples of 1.5 g mass were loaded into a sample holder having a thermocouple located at the center of the sample. Temperatures and pressures during the sorption process were monitored in both sample space and gas reservoirs and recorded by a Labview-based control program.

3. Results and discussion

3.1. Intermetallic NdCo$_3$NiB (uncycled and cycled):

For NdCo$_4$B and NdCo$_3$NiB (cycled and uncycled) the X-ray powder diffraction patterns are consistent with the expected CeCo$_4$B-type structure (space group is $P6/mmm$). The refined cell parameters and free atomic parameter of NdCo$_4$B ($a = 5.1067(3)$, $c = 6.8893(6)$ Å, z(Co2(6i)) = 0.2886(5) are in good agreement with those published [18], albeit of higher accuracy in our study (data not shown here). For NdCo$_3$NiB the Nd atoms occupy the 1a and 1b sites and B occupies the 2d site, while Co and Ni appear to randomly distributed over the 2c (T1) and 6i (T2) sites. A possible deviation from random occupancy cannot be deduced from X-ray data, given the similar X-ray scattering powers of cobalt and nickel, but could be deduced from neutron data, given their significantly different coherent neutron scattering lengths (Co: 2.49 fm; Ni: 10.3 fm) [19].

The structure refinements of the neutron data were performed in the following steps: firstly, an overall isotropic Atomic Displace-ment Parameter (ADP) was refined and then fixed; secondly the ADPs of cobalt and nickel on the same site were constrained to be equal, and the site occupancies and ADPs of T1 and T2 were refined separately; finally both types of parameters were refined simul-taneously by fixing the overall compositional ratio of the T1 and T2 sites to Co/Ni = 3. The results for cycled and uncycled NdCo$_3$NiB are summarized in Table 1. Clearly, the occupancies of the metal sites give no indication for a hydrogen induced Co/Ni ordering, at least after three hydrogen absorption–desorption cycles. While the occupancy ratios between the two transition-metal sites T1 and T2 differ significantly (that of T1 (65%Co/35%Ni) has less Co and that of T2 (78%Co/22%Ni) has more Co than expected for ran-dom distributions, as expected from similar behavior in CaNi$_5$–type substitution derivatives, and in good agreement with the atomic radii (r[Co] = 1.252 Å (C.N. = 12) and r[Ni] = 1.246 Å (C.N. = 12)) [20]), these ratios are not affected by cycling.

3.2. Uncyled and cycled deuterides NdCo$_3$NiBD$_x$:

Attempts to refine the structures of the deuterides in the cen-trosymmetric space-group P6/mmm were unsuccessful, whereas, the structure described in $P6mm$ space-group shows excellent agreement between experimental and calculated neutron pow-der intensities. As deuterium-induced decrease of symmetry was already described in the literature for LaNi$_5$, from $P6/mmm$ for LaNi$_5$ to $P6mm$ for LaNi$_5$D$_5$ [21], and from $P6/mmm$ for LaNi$_5$ to $P31m$ for LaNi$_5$D$_6$ [22], an attempt to refine the structure was also performed in $P31m$ (and in others lower symmetries), whereas poor conver-gences were achieved. The losses of the mirror perpendicular to the c-axis as well as the centre of symmetry are associated with the following relations of the Wyckoff positions during transfor-mations from $P6/mmm$ to $P6mm$: Co(6i) site splits into two Co(3c) sites and D(12o) site splits into two D(6e) sites. A total of three

Table 2
Refinement results for uncycled $NdCo_3NiBD_{2.99}$ (top) and cycled $NdCo_3NiBD_{3.44}$ (bottom) from neutron measurements at $T = 373$ K, space group $P6mm$; * fixed; $T = Co + Ni$; occupancy factors of cobalt and nickel on same site constrained to 1.0.

Atoms	Site	x	y	z	B (Å^2)	Occ.
$NdCo_3NiBD_{2.99}$ (uncycled)[a]						
Nd1	1a	0	0	0(−)*	1.48(9)	1.0
Nd2	1a	0	0	0.501(1)	0.82(6)	1.0
T1	2b	1/3	2/3	0.041(1)	1.11(9)	0.71(1) + 0.29(1)
T2	3c	½	0	0.334(1)	0.88(7)	0.77(1) + 0.23(1)
T3	3c	½	0	0.713(1)	1.12(9)	0.75(2) + 0.25(2)
^{11}B	2b	1/3	2/3	0.523(1)	0.50(4)	1.0
D1	6e	0.813(1)	0.187(1)	0.217(1)	2.00(4)	0.40(2)
D2	3c	½	0	0.943(1)	2.00(4)	0.81(2)
D3	6e	0.150(2)	0.850(2)	0.744(2)	2.00(4)	0.19(3)
$NdCo_3NiBD_{3.44}$ (cycled)[b]						
Nd1	1a	0	0	0(−)*	0.9(1)	1.0
Nd2	1a	0	0	0.516(2)	1.0(1)	1.0
T1	2b	1/3	2/3	0.047(2)	1.1(2)	0.75(1) + 0.25(1)
T2	3c	½	0	0.341(2)	0.6(1)	0.85(2) + 0.15(2)
T3	3c	½	0	0.721(2)	1.7(1)	0.65(2) + 0.35(2)
^{11}B	2b	1/3	2/3	0.537(2)	0.1(1)	1.0
D1	6e	0.815(1)	0.185(1)	0.225(2)	1.9(1)	0.52(4)
D2	3c	½	0	0.950(2)	1.9(1)	0.79(3)
D3	6e	0.138(2)	0.862(2)	0.756(3)	1.9(1)	0.23(4)

[a] $a = 5.2786(3)$ Å, $c = 7.2675(5)$ Å, $V = 175.37(2)\,\text{Å}^3$, $Z = 2$, $R_{Bragg} = 6.75\%$, $R_{wp} = 12.6\%$, $\chi^2 = 4.33$; refined composition $NdCo_3NiBD_{2.99}$
[b] $a = 5.2801(2)$ Å, $c = 7.2923(5)$ Å, $V = 176.06(2)\,\text{Å}^3$, $Z = 2$, $R_{Bragg} = 10.5\%$, $R_{wp} = 7.92\%$, $\chi^2 = 6.28$; refined composition $NdCo_3NiBD_{3.44}$

D atom sites were located on nuclear difference density Fourier maps which were in agreement with those found by the program FOX [23]. $P6mm$ being a polar space-group, the z-coordinate of Nd1 was fixed to zero. The background was modeled by interpolation coupled with a Fourier filtering treatment, and the overall T metal composition on the 3 T metal sites was restrained to Co/Ni = 3. The refinement results for uncycled and cycled $NdCo_3NiBD_x$ are summarized in Table 2 (data for $NdCo_4B$ not shown here), and a list of short boron-metal, boron-deuterium, deuterium-metal, and deuterium-deuterium distances is given in Table 3. A structural drawing including a comparison with $LaNi_5D_7$ is given in Fig. 1, and the metal coordinations around the D atom sites are represented in Fig. 2. The refined deuterium occupancies suggest slightly different compositions, $NdCo_3NiBD_{2.99}$ and $NdCo_3NiBD_{3.44}$ for uncycled and cycled sample, respectively. This difference correlates with the cell volumes and is consistent with the fact that the data for the uncycled sample were collected under hydrogen pressure on the *in situ* line, whereas those of the cycled sample were collected *ex*

Table 3
Shortest boron-metal, boron-deuterium, deuterium-metal, and deuterium-deuterium distances (Å) in uncycled $NdCo_3NiBD_{2.99}$ (left) and cycled $NdCo_3NiBD_{3.44}$ (right); e.s.d.'s in parentheses.

|		Uncycled $NdCo_3NiBD_{2.99}$	Cycled $NdCo_3NiBD_{3.44}$
B-	3Nd2	3.052(1)	3.052(1)
	T1	3.503(10)	3.573(21)
	3T2	2.052(7)	2.090(14)
	3T3	2.056(7)	2.031(14)
	3D1	2.595(9)	2.649(18)
	3D3	2.321(14)	2.396(14)
D1-	Nd1	2.326(7)	2.357(11)
	Nd2	2.680(9)	2.714(17)
	T1	1.851(8)	1.878(15)
	2T2	1.672(6)	1.677(11)
	2D1	1.710(7)	1.692(6)
D2-	2Nd1	2.672(11)	2.665(2)
	2T1	1.682(4)	1.680(9)
	T3	1.672(10)	1.670(21)
	4D3	2.161(13)	2.189(19)
D3-	Nd1	2.311(14)	2.181(19)
	Nd2	2.236(15)	2.158(23)
	2T3	1.621(10)	1.690(11)
	2D3	1.371(13)	1.262(13)
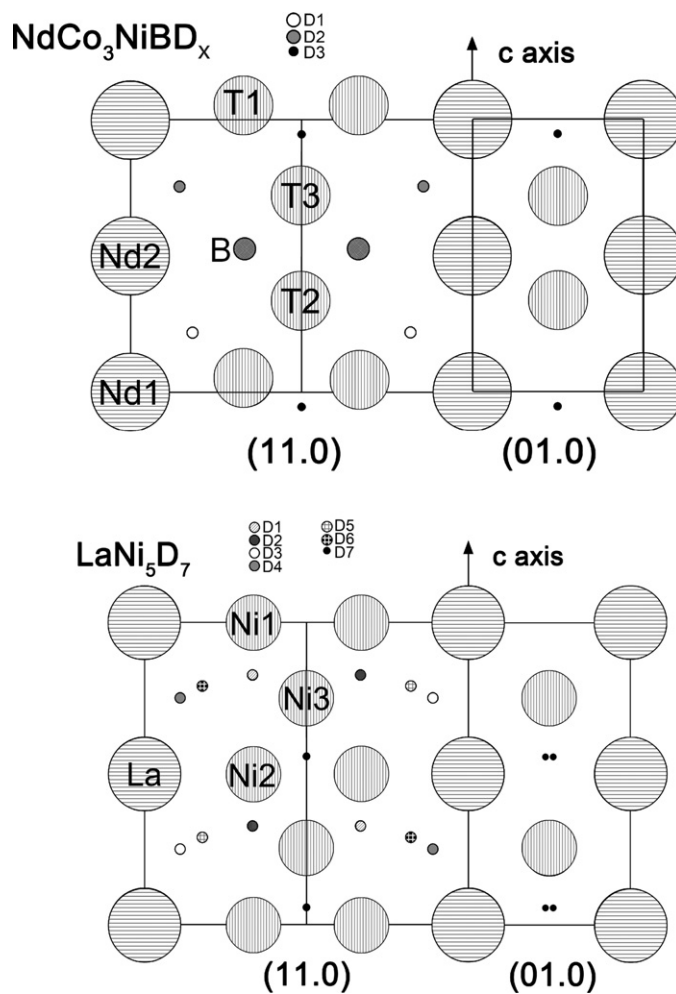
Fig. 1. Atom positions of $NdCo_3NiBD_x$ (space group $P6mm$) in hexagonal (11.0) and (01.0) planes as compared to $LaNi_5D_7$ (7-site model, space group $P6_3mc$, atom labels from [21]).
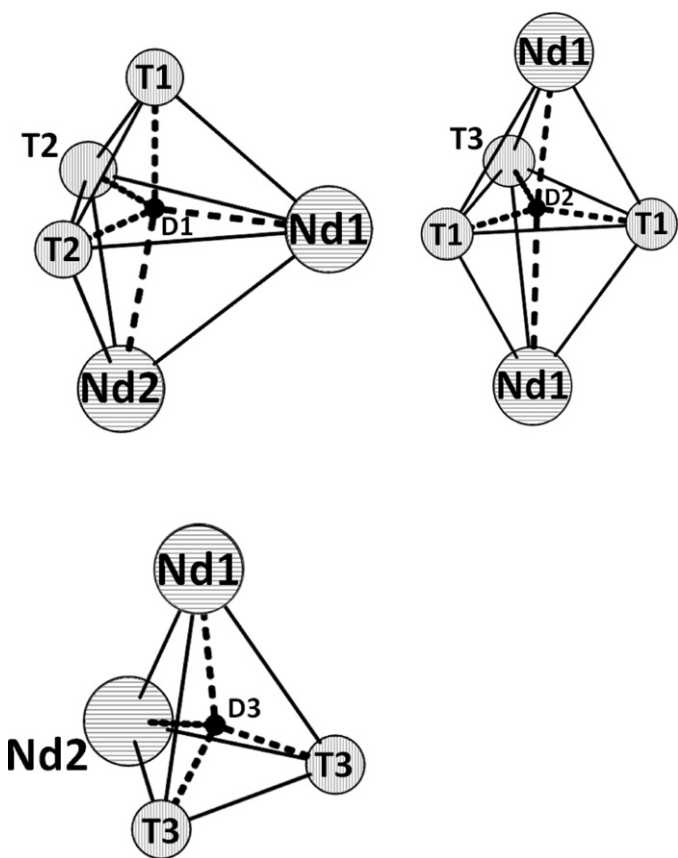
Fig. 2. Metal coordinations of deuterium atoms in $NdCo_3NiBD_x$.

Fig. 3. Pressure-composition isotherm of $NdCo_3NiB$–H system at 303 K.

situ under atmospheric pressure, leading to a possible desorption of the deuteride.

As with D-free $NdCo_3NiB$ the various T-metal sites show significantly different Co/Ni ratios, but these ratios do not change much upon cycling in hydrogen. Thus there exists again no indication for a H-induced T-metal ordering. As to the influence of boron on the D atom distribution the following observations can be made. Firstly, the metal coordination polyhedra around the D sites in $NdCo_3NiBD_x$ are quite different from those in $LaNi_5D_7$. As shown in Figs. 1 and 2 and the table of interatomic distances (Table 3) D1 and D2 have trigonal bi-pyramidal metal coordinations Nd_2T_3, while D3 has tetrahedral metal coordination Nd_2T_2. Thus, none of the deuterium sites in the boride has close boron atoms, in contrast to many deuterium sites in $LaNi_5D_7$ that are coordinated by those Ni atoms which are substituted by boron in the boride. Specifically, site D1 in the boride corresponds to site D1 (or D3) in $LaNi_5D_7$ having tetrahedral coordination La_2Ni_2, to which one transition metal atom (T1) has joined the coordination, thus yielding a trigonal-bipyramidal coordination of type Nd_2T_3. Site D2 in the boride comes close to site D7 in $LaNi_5D_7$ having sixfold coordination La_2Ni_4. However, one of the T atoms (T2) has left the coordination in the boride, thus yielding a trigonal bi-pyramidal environment of type Nd_2T_3. The tetrahedrally coordinated site D3 in the boride corresponds to site D3 (or D1) in $LaNi_5D_7$ having tetrahedral coordination La_2Ni_2. All D-metal distances are in the usual range (D-Nd = 2.3–2.7 Å; D-T = 1.6–1.9 Å). As to the B-D distances (2.6 Å for D1, 2.3 Å for D3) they are too long for bonding interactions and rather indicate repulsive B-D interactions. Boron interacts mainly with transition elements (2.1 Å for T2) and neodymium (2.9 Å for Nd2). Deuterium-deuterium contacts less than 2 Å occur only between sites whose occupancies add up to less than unity and thus are consistent with repulsive D-D interactions.
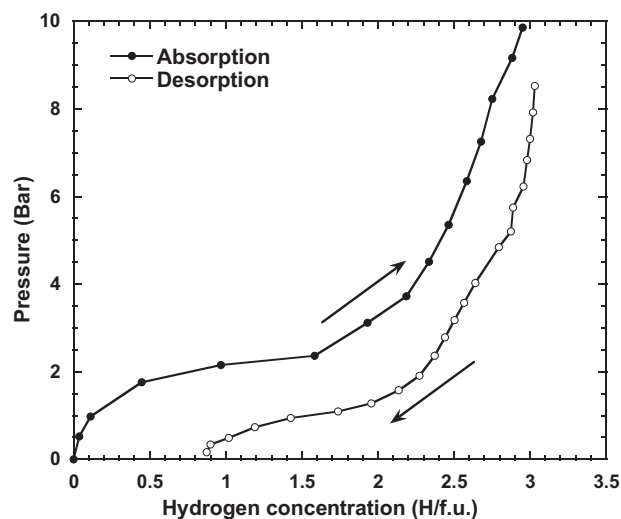
3.3. PCI measurements

$NdCo_3NiB$ was activated by three hydrogen absorption–desorption cycles as follows: first, the reactor containing the intermetallic compound was heated at 373 K for two days under dynamic vacuum, then it was charged with 60 bar of hydrogen, and finally kept for three days under these conditions. This cycle was repeated three times. PCT data were then recorded during absorption and desorption at 303 K. As shown in Fig. 3 the data exhibit a single equilibrium plateau pressure, corresponding to a $\alpha + \beta$ two-phase region around 2 bar. A maximum hydrogen storage capacity of around 3.1 hydrogen atoms per formula unit was obtained at 10 bar and 303 K, which is in good agreement with the value obtained from the neutron structure refinement.

The isotherms of non-stoichiometric $NdNi_5$ exhibit two well separated pressure plateau regions at 293 K [24]. The equilibrium pressure of the first plateau for the non-stoichiometric $NdNi_{4.8}$ is lower than the corresponding values for binary $NdNi_5$. In [25], $NdNi_5$ presents at 298 K two hydrides having compositions of $NdNi_5H_{\sim4}$ and $NdNi_5H_{\sim6.2}$. $NdCo_5$ absorbs a maximum of 3.7 H atom per formula unit [26]. In our compound, only one plateau pressure is observed at 303 K. Addition of boron tends to reduce the hydrogen capacity and decreases also the equilibrium pressure of the second plateau shown for the binary $NdNi_5$.

Kinetics are rather slow (one week for the whole absorption cycle). Spada et al. [2] noticed similar slow kinetics of absorption and desorption for the isostructural nickel compounds $LaNi_4B$ and $PrNi_4B$ but not for the cobalt compounds $LaCo_4B$ or $PrCo_4B$. Clearly, desorption of the $NdCo_3NiB$–H system at 303 K and 0.1 bar is not complete, but full desorption can be achieved by heating to 473 K, as confirmed by X-ray powder diffraction.

Acknowledgements

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