

# Interaction of hydrogen with $\text{RECu}_2$ and $\text{RE}(\text{Cu},\text{Ni})_2$ intermetallic compounds ( $\text{RE}=\text{Y}, \text{Pr}, \text{Dy}, \text{Ho}$ )<sup>☆</sup>

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## Abstract

Hydrogenation of  $\text{RECu}_2$  ( $\text{RE}=\text{Dy}, \text{Ho}, \text{Y}$ ) at room temperature and pressures of 100–1500-bar  $\text{H}_2$  has not resulted in the formation of ternary hydrides. The interaction of hydrogen with  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  ( $x=0, 0.1, 0.17, 0.25, 0.32$ ) at room temperature and pressure of 25 bar resulted in the formation of  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{H}_{-3}$  hydrides. It was found that the  $\text{PrCu}_2\text{H}_3$  and  $\text{Pr}(\text{Cu}_{0.9}\text{Ni}_{0.1})_2\text{H}_{2.9}$  hydrides are poorly crystallized, but that an increase of the Ni-content leads to improved crystallinity of the hydrides. The hydrides  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{-3}$  and  $\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{-3}$  preserve, shortly after the hydrogen absorption, the  $\text{CeCu}_2$  type structure of their metallic matrix with a hydrogen induced volume expansion up to 28% compared to the parent compound. During long-term exposure in the air they undergo a structural transformation from the orthorhombic  $\text{CeCu}_2$  to the hexagonal  $\text{Fe}_2\text{P}$  type with a hydrogen induced volume expansion up to 16.6% compared to the parent compound.

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## 1. Introduction

$\text{RET}_2$  ( $\text{RE}=\text{Y}$ , rare earth;  $\text{T}=\text{Fe}, \text{Co}, \text{Ni}$ ) cubic Laves phases ( $\text{MgCu}_2$  type structure,  $Fd\bar{3}m$  [1]) easily form  $\text{RET}_2\text{H}_{3-4.5}$  hydrides. Depending on the conditions, the hydrogenation results either in formation of crystalline or amorphous hydrides, or in disproportionation into a mixture of binary  $\text{REH}_x$  hydride and another intermetallic compound [2–5]. The crystalline hydrides have the same cubic structure of the metal matrix as the parent Laves phases and a substantially expanded unit cell volume (up to  $\Delta V/V=29\%$ ). In some cases hydride formation is accompanied by an orthorhombic [6] or tetragonal [7] distortion of the metal matrix.

In contrast, little is known about the hydrogenation

properties of  $\text{RECu}_2$  compounds, which crystallize with orthorhombic ( $Imma$ )  $\text{KHg}_2$  type structure [8], also called  $\text{CeCu}_2$  type structure [9]. The hydrogenation of  $\text{SmCu}_2$  has resulted in a disproportionation into  $\text{SmH}_2$  and  $\text{Cu}$  [10]. The formation of a crystalline hydride phase, which is accompanied by a structural transformation from the  $\text{CeCu}_2$  type structure to the tetragonal  $\text{MoSi}_2$  type ( $I4/mmm$  [11]), has been reported for the  $\text{GdCu}_2$  compound [12].

In this work we present results of hydrogenation studies of binary  $\text{RECu}_2$  compounds ( $\text{RE}=\text{Y}, \text{Pr}, \text{Dy}$  and  $\text{Ho}$ ) and pseudobinary  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds.

## 2. Experimental

The parent alloys were prepared from pure elements ( $\text{RE}>99.8\%$ ;  $\text{Cu } 99.99\%$ ;  $\text{Ni } 99.95\%$ ) by arc melting in a purified argon atmosphere on a water-cooled copper hearth. The samples were annealed in evacuated quartz tubes at  $800^\circ\text{C}$  for 2 weeks and quenched into ice water afterwards.

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The hydrides were prepared at room temperature by exposing the samples to different hydrogen pressures in the range from 25 up to 1500 bar, in some cases using the admixtures with an easily hydrogenating alloy ( $\text{LaNi}_5$ ) as a catalyst. The amount of absorbed hydrogen was measured by the volumetric technique using a Sieverts type apparatus for  $\text{H}_2$  pressure up to 100 [13] and 1500 bar [14].

All parent alloys and corresponding hydrides were characterized by X-ray powder diffraction. The X-ray powder patterns were collected with a Bruker D8 (Cu  $\text{K}\alpha_1$  radiation) and DRON-3.0 (Cu  $\text{K}\alpha$  radiation) diffractometers. FULLPROF [15] and CSD [16] programs were used for the Rietveld refinement.

### 3. Results and discussion

Analysis of X-ray powder patterns of all binary parent alloys revealed the formation of nearly single phase samples with  $\text{CeCu}_2$  type structure compounds as the main phase (Table 1).

Hydrogenation of the  $\text{HoCu}_2$  and  $\text{YCu}_2$  compounds at room temperature and at pressures of 150 and 1500 bar did not result in the formation of ternary hydrides.  $\text{DyCu}_2$  when hydrogenated at room temperature and at a hydrogen pressure of 100 bar did not form a ternary hydride, but disproportionated into dysprosium dihydride and copper upon heating. It is known [17] that the admixtures of a catalytic quantity of an easily hydrogenating compound (e.g.  $\text{LaNi}_5$ ) can be used to enhance the hydrogenation of an alloy, which has a lower affinity to hydrogen. In this case the hydrogen gas interacts with  $\text{LaNi}_5$  and then atomic hydrogen diffuses through the contact interface between both alloys to the last constituent of this mixture. In this work the hydrogenation of  $\text{PrCu}_2$  with a catalytic quantity of  $\text{LaNi}_5$  under 25 bar of hydrogen gas resulted in the formation of  $\text{PrCu}_2\text{H}_{\sim 3}$  hydride, which was character-

ized by X-ray diffraction as a poorly crystallized or amorphous phase.

Looking for better hydrogenation conditions and crystallinity of the hydrides, we have prepared a series of Ni-substituted  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds ( $x=0.1, 0.17, 0.25$  and  $0.32$ ). As revealed by X-ray powder diffraction (Fig. 1a) all Ni-substituted compounds retain the orthorhombic  $\text{CeCu}_2$  type structure. A possible ordering of the copper and nickel atoms on the  $8h$  Wyckoff site of the  $\text{CeCu}_2$  type structure cannot be elucidated from the X-ray data due to the low diffraction contrast between these two elements. Partial replacement of Cu atoms by the smaller Ni atoms ( $r_{\text{Cu}}=1.278$  and  $r_{\text{Ni}}=1.246$  Å) is reflected in the changes of lattice parameters: with increasing Ni-content the lattice parameters  $a$ ,  $c$  and the unit cell volume  $V$  decrease, whereas the lattice parameter  $b$  increases (Fig. 2).

Hydrogenation of  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  alloys at room temperature under 25-bar hydrogen pressure has resulted in the formation of hydrides with a hydrogen content of 2.9–3.1 H/f.u. The samples with the composition  $\text{Pr}(\text{Cu}_{0.9}\text{Ni}_{0.1})_2\text{H}_{2.9}$  and  $\text{Pr}(\text{Cu}_{0.83}\text{Ni}_{0.17})_2\text{H}_{2.9}$  appeared to be very poorly crystallised. However, further increase of the Ni-content substantially improves the crystallinity of the hydride phases. In the case of  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_3$  and  $\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{3.1}$  the Rietveld refinement using the X-ray powder data of freshly charged hydrides has revealed the formation of a hydride phase where the metallic matrix has preserved the  $\text{CeCu}_2$  type structure with a unit cell volume expansion up to 28% (Fig. 1b and Table 1). The results of the Rietveld refinement of these samples are not shown here, because of the low quality of the data. However, they were used when preparing Fig. 4. This volume increase is close to the lattice expansion observed during the hydrogenation of  $\text{GdCu}_2$  (27%), which, as mentioned above, was accompanied by a structural change from the  $\text{CeCu}_2$  type structure to the  $\text{MoSi}_2$  type [12]. The lattice expansion in our case occurs mainly along the  $b$  and

Table 1  
Lattice parameters and cell volume of the parent  $\text{RE}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds and their hydrides

Compound	Structure type of the metal matrix	Lattice parameters (Å)			V (Å <sup>3</sup> )	$\Delta V/V^a$ (%)
		a	b	c		
$\text{YCu}_2$	$\text{CeCu}_2$	4.300(4)	6.839(7)	7.287(6)	214.3(6)	–
$\text{DyCu}_2$	$\text{CeCu}_2$	4.297(1)	6.789(3)	7.290(3)	212.7(2)	–
$\text{HoCu}_2$	$\text{CeCu}_2$	4.2883(3)	6.778(1)	7.278(1)	211.5(1)	–
$\text{PrCu}_2$	$\text{CeCu}_2$	4.4071(8)	7.054(1)	7.440(1)	231.3(1)	–
$\text{Pr}(\text{Cu}_{0.9}\text{Ni}_{0.1})_2$	$\text{CeCu}_2$	4.3854(7)	7.065(1)	7.412(1)	229.6(1)	–
$\text{Pr}(\text{Cu}_{0.83}\text{Ni}_{0.17})_2$	$\text{CeCu}_2$	4.370(1)	7.077(2)	7.380(2)	228.3(2)	–
$\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2$	$\text{CeCu}_2$	4.3594(6)	7.085(1)	7.357(1)	56.8(1) <sup>b</sup>	–
$\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0}$	$\text{CeCu}_2$	4.443(4)	8.228(5)	7.931(7)	72.5(2) <sup>b</sup>	27.6
$\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0-x}$	$\text{Fe}_2\text{P}$	7.5916(4)	–	3.9798(1)	66.21(1) <sup>b</sup>	16.6
$\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2$	$\text{CeCu}_2$	4.3455(7)	7.092(1)	7.341(1)	56.48(1) <sup>b</sup>	–
$\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{3.1}$	$\text{CeCu}_2$	4.418(1)	8.200(3)	7.981(2)	72.3(1) <sup>b</sup>	28.0
$\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{3.1-x}$	$\text{Fe}_2\text{P}$	7.528(2)	–	3.928(1)	64.3(1) <sup>b</sup>	13.8

<sup>a</sup> Volume increase for hydrogenated samples.

<sup>b</sup>  $\Delta V/V$ , volume per formula unit' was calculated in order to compare the hydrogen-induced expansion for  $\text{CeCu}_2$  and  $\text{Fe}_2\text{P}$  structure type hydrides.

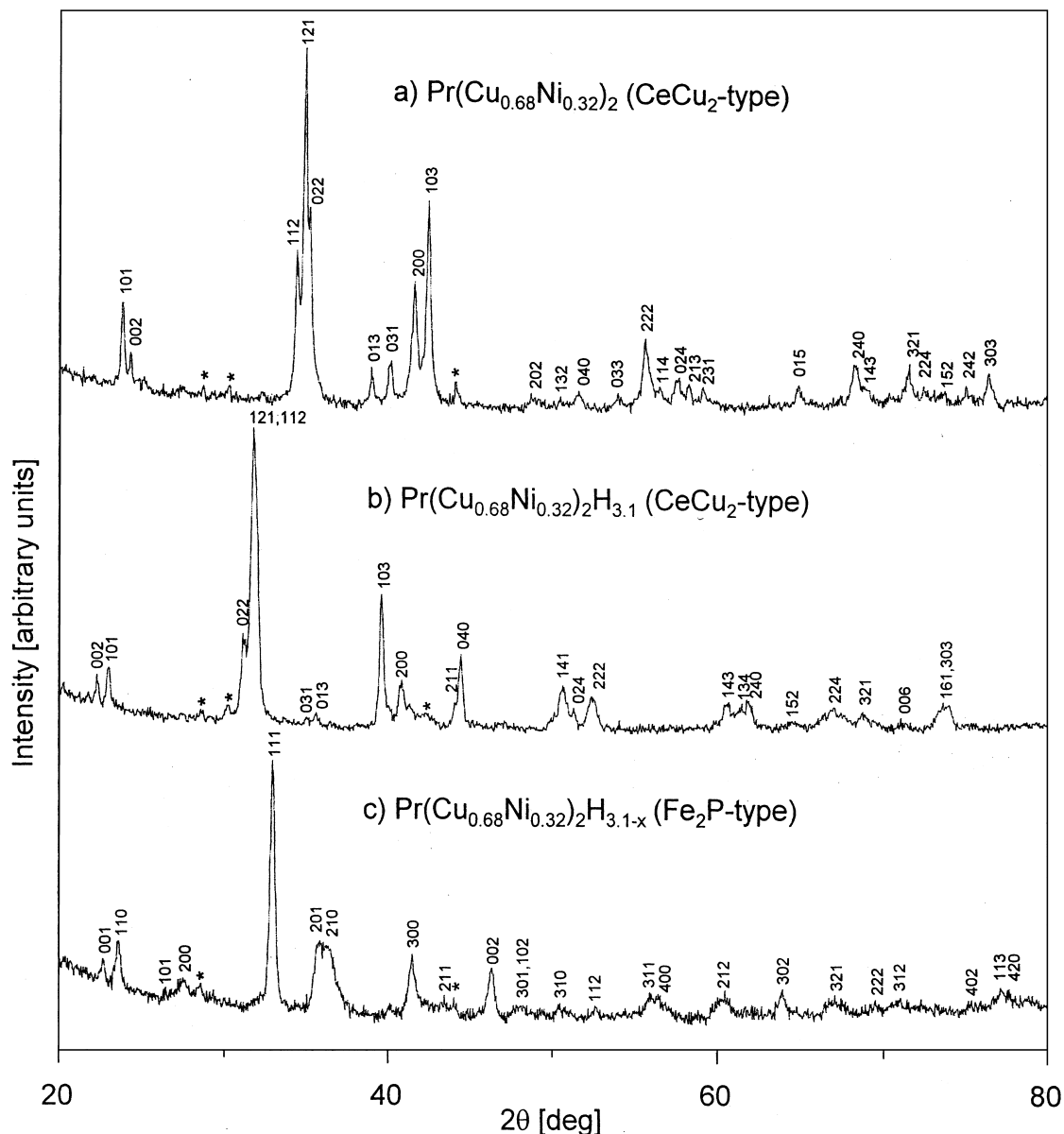


Fig. 1. X-ray powder diffraction patterns of: (a)  $\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2$  parent compound with the  $\text{CeCu}_2$  type structure, (b) freshly synthesized hydride keeping the  $\text{CeCu}_2$  type structure for the metal matrix, (c) the same hydride after long-term exposure in the air with the  $\text{Fe}_2\text{P}$  type structure of the metal matrix. Peaks of the secondary phase  $\text{Pr}(\text{Cu,Ni})_5$  and its hydride are marked by (\*).

$c$  axes of the orthorhombic unit cell  $\Delta b/b = \sim 16\%$ ,  $\Delta c/c = \sim 8.5\%$ . The  $a$  parameter remains almost unchanged,  $\Delta a/a = \sim 1.8\%$ .

After keeping both hydrides,  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_3$  and  $\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{3.1}$ , outside the reactor during 1 month we have observed completely different X-ray powder patterns (Fig. 1c), where the main phase was indexed in a hexagonal unit cell and attributed to the  $\text{Fe}_2\text{P}$  structure type ( $P\bar{6}2m$ ) [18]. Rietveld refinement was performed for one of these samples, namely  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_3$  (Fig. 3 and Table 2). In addition to the main phase  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3-x}$ , a small quantity (4.85%) of the  $\text{Pr}(\text{Cu,Ni})_5\text{H}_y$  phase has been detected. The obtained results demonstrate that the main phase

$\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3-x}$  is a substitution derivative of the  $\text{Fe}_2\text{P}$  type structure. The RE atom occupies the  $3g$  position instead of the  $1b$  and  $2c$  positions for the phosphorus atoms in  $\text{Fe}_2\text{P}$ . A possible ordering of the copper and nickel atoms on the  $1b$ ,  $2c$  and  $3f$  Wyckoff sites of the  $\text{Fe}_2\text{P}$  structure type cannot be elucidated from the X-ray data due to the low diffraction contrast between these two elements.

The hydrogenation-induced expansion of the metallic matrix of this hexagonal hydride is almost twice smaller than that of the freshly prepared hydride that keeps the  $\text{CeCu}_2$  type of structure. Therefore a partial release of hydrogen from the  $\text{CeCu}_2$  hydride can be supposed as a possible mechanism for the  $\text{CeCu}_2 \rightarrow \text{Fe}_2\text{P}$

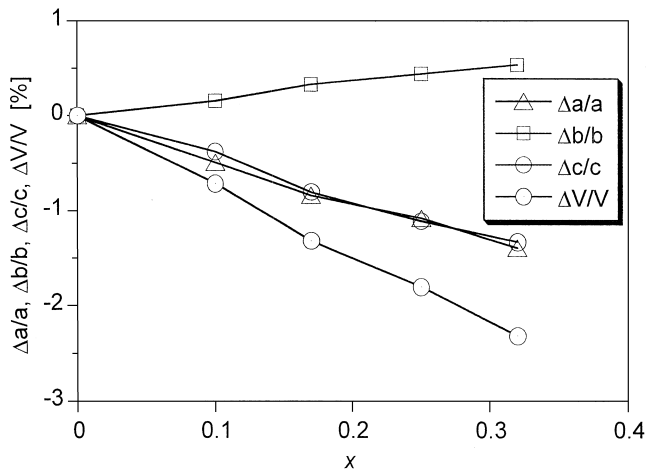


Fig. 2. Effect of Ni substitution on the lattice parameters and the cell volume of the  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compound with the  $\text{CeCu}_2$  type structure.

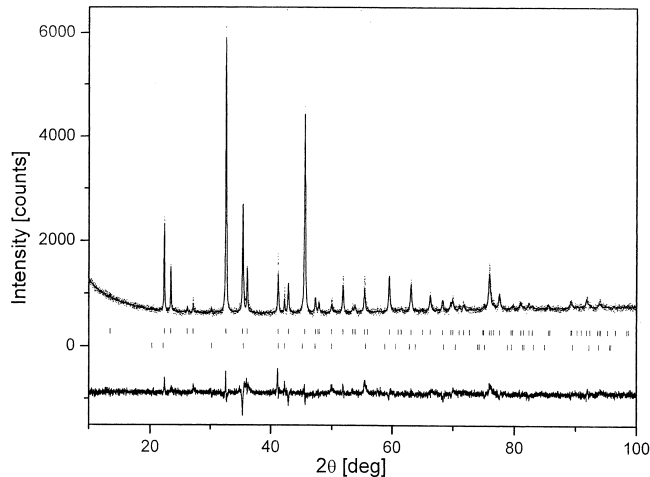


Fig. 3. X-ray powder diffraction patterns from the Rietveld refinement of the  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0-x}$  hydride (25 °C,  $\text{Cu K}\alpha_1$ ): observed (+), calculated (line), difference (bottom line). Positions of Bragg's peaks for  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0-x}$  (top) and  $\text{Pr}(\text{Cu,Ni})_5\text{H}_y$  (bottom) are also given.

Table 2

Crystallographic data for  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0-x}$  hydride

Atom	Site	$x/a$	$y/b$	$z/c$	$B$ ( $\text{\AA}^2$ )
Pr	3g	0.6137(3)	0	1/2	0.19(6)
T1 <sup>a</sup>	2c	1/3	2/3	0	$=B_{\text{Pr}}$
T2 <sup>a</sup>	1b	0	0	1/2	$=B_{\text{Pr}}$
T3 <sup>a</sup>	3f	0.212(1)	0	0	$=B_{\text{Pr}}$

Space group:  $P\bar{6}2m$ . Lattice parameters:  $a=7.5899(4)$ ;  $c=3.9786(2)$   $\text{\AA}$ . Cell volume:  $V=198.49(2)$   $\text{\AA}^3$ .  $R_{\text{wp}}$  (background corrected)=26.6%,  $\chi^2=2.43$ . Background estimated manually in 24 points. Refined parameters for the main phase: one scale, two lattice, eight profile, three atomic, one preferred orientation (001). In addition to the main phase  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3.0-x}$  (95.15 wt.%), a small quantity (4.85%) of the  $\text{Pr}(\text{Cu,Ni})_5\text{H}_y$  phase ( $P6/mmm$ ;  $a=5.0514(9)$ ;  $c=4.013(3)$   $\text{\AA}$ ) was observed.

<sup>a</sup>  $\text{T}=\text{Cu}_{0.75}\text{Ni}_{0.25}$ .

transition. Therefore these  $\text{Fe}_2\text{P}$  type hydrides are marked in this paper as  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{3-x}$  and  $\text{Pr}(\text{Cu}_{0.68}\text{Ni}_{0.32})_2\text{H}_{3.1-x}$ . On the other hand, the  $\text{CeCu}_2$  type hydride can be a structurally metastable phase with a kinetically decelerated  $\text{CeCu}_2 \rightarrow \text{Fe}_2\text{P}$  transformation. This can be supposed if account is taken of the values of unit cell increment per H atom absorbed. It is rather large for the  $\text{CeCu}_2$  type hydrides ( $\sim 5.3 \text{\AA}^3$ ) and within the commonly observed 2–3  $\text{\AA}^3$  range for the  $\text{Fe}_2\text{P}$  type hydrides ( $\sim 2.9 \text{\AA}^3$ ).

The relation between the  $\text{CeCu}_2$  and  $\text{Fe}_2\text{P}$  type structures is illustrated in Fig. 4. During the hydrogenation of the  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  compounds with  $\text{CeCu}_2$  type structure the puckered net of T (Cu+Ni) atoms (Fig. 4a) becomes almost planar with a thickness of  $\sim 0.08 \text{\AA}$  (Fig. 4b). It creates the preconditions for 6-fold symmetry axes upon further transformation into the  $\text{Fe}_2\text{P}$  type of structure (Fig. 4c). If the ratio  $c/a$  between the lattice parameters of the  $\text{CeCu}_2$  type structure were equal to  $\text{SQRT}(3)$  then the structure type would be the trigonal  $\text{EuGe}_2$ , and if further the net of T atoms became exactly planar, the structure type would be hexagonal  $\text{AlB}_2$  ( $P6/mmm$  [19]), related to the  $\text{CeCu}_2$  type. Also the  $\text{Fe}_2\text{P}$  type is very closely related to the  $\text{AlB}_2$  type. However, it cannot be derived directly by a group-subgroup relation, because the atomic position corresponding to the Wyckoff site 1b of the  $\text{Fe}_2\text{P}$  type (atom T2) is not occupied in the  $\text{AlB}_2$  type. The position that is occupied instead in the  $\text{AlB}_2$  type and that is empty in the  $\text{Fe}_2\text{P}$  type corresponds to the Wyckoff site 1a of the  $\text{Fe}_2\text{P}$  type. Upon transition of the metal matrix from the  $\text{CeCu}_2$  to the  $\text{Fe}_2\text{P}$  type, the T2 atoms move by  $\sim 2 \text{\AA}$  from the T-plane into the Pr-plane (Fig. 4b,c). These relations demonstrate that the hydrogenation induces smooth structural transformations and that the structure types of parent and hydrogenated intermetallic compounds are closely related. Neutron powder diffraction analysis is planned to describe fully the structure of the deuterated compounds.

#### 4. Conclusions

Hydrogenation of  $\text{RECu}_2$  (RE=Dy, Ho, Y) at room temperature and pressures of 100-, 150- and 1500-bar  $\text{H}_2$  has not resulted in the formation of ternary hydrides.  $\text{DyCu}_2$  decomposes into a mixture of  $\text{DyH}_2$  and copper upon heating. The existence of a  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  solid solution up to  $x=0.32$  in the ternary system has been revealed. The interaction of hydrogen with  $\text{PrCu}_2$  and  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2$  ( $x=0.1, 0.17, 0.25, 0.32$ ) by gradual increase of pressure from 0 to 25 bar resulted in the formation of  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{H}_{\sim 3}$  hydrides. It was found that  $\text{PrCu}_2\text{H}_3$  and  $\text{Pr}(\text{Cu}_{0.9}\text{Ni}_{0.1})_2\text{H}_{2.9}$  hydrides are amorphous or poorly crystallized, but the increase in Ni content leads to an improvement of the crystallinity of the hydrides. The hydrides  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{\sim 3}$  and  $\text{Pr}(\text{Cu}_{0.75}\text{Ni}_{0.25})_2\text{H}_{\sim 3}$  preserve, just after the hydrogen absorption, the symmetry

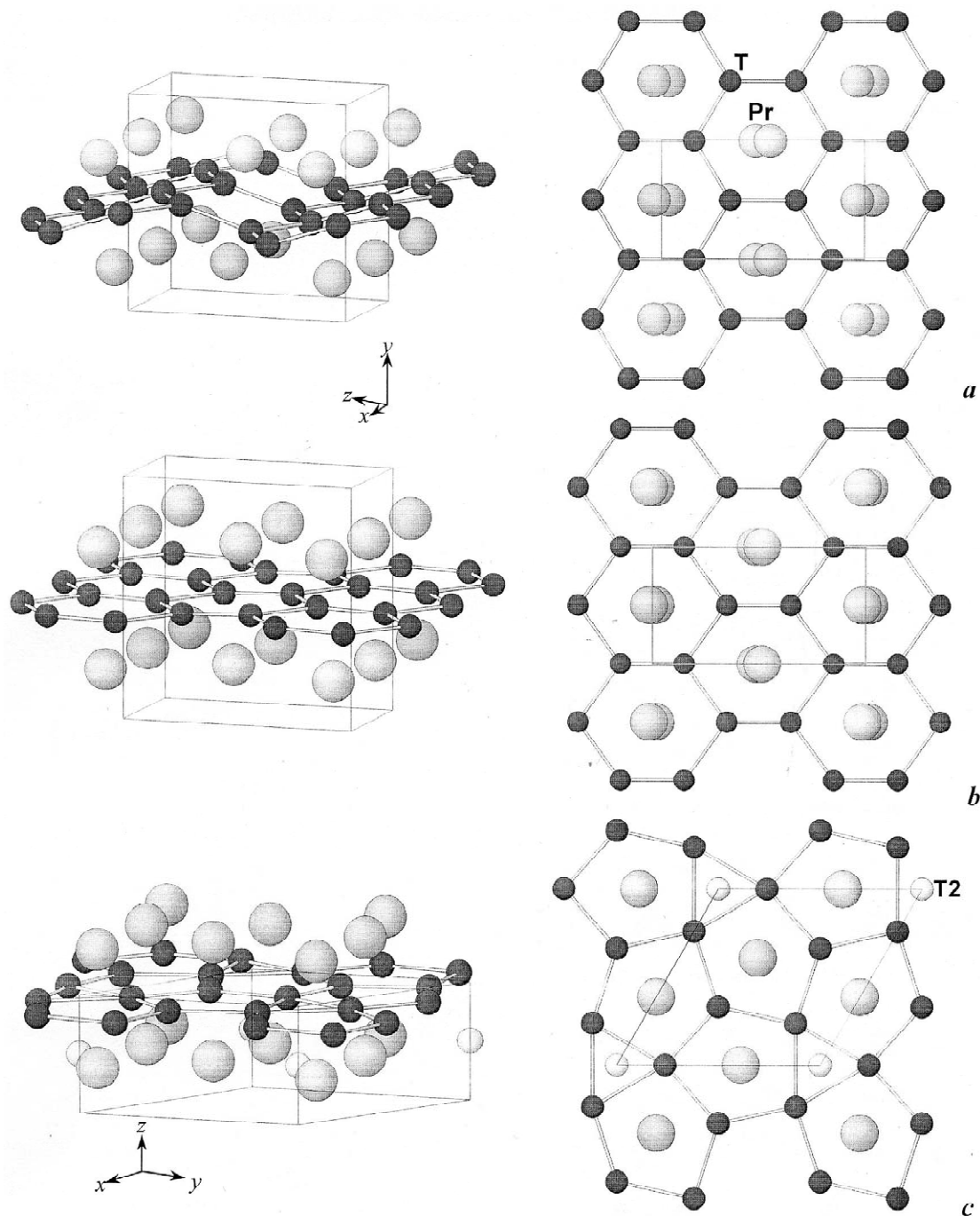


Fig. 4. Nets of T (Cu+Ni) and Pr atoms (left column) and their projections along the pseudo-hexagonal/hexagonal axis (right column) for parent  $\text{Pr}(\text{Cu}_x\text{Ni}_{1-x})_2$  with the  $\text{CeCu}_2$  type structure (a), its  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{H}_{3-3x}$  hydride with the preserved  $\text{CeCu}_2$  type structure of the metal matrix (b) and the  $\text{Pr}(\text{Cu}_{1-x}\text{Ni}_x)_2\text{H}_{3-3x}$  hydride with the  $\text{Fe}_2\text{P}$  type structure of the metal matrix (c).

of their metallic matrix and show a unit cell volume expansion up to 28%. These hydrides undergo a crystal structure transformation from the orthorhombic  $\text{CeCu}_2$  type to the hexagonal  $\text{Fe}_2\text{P}$  type during long-term exposure in the air. The hydrogen-induced expansion of the metallic matrix of this hexagonal hydride is almost twice smaller than that of the freshly prepared hydride of  $\text{CeCu}_2$  type structure. A partial hydrogen release upon keeping in the

air is probably the mechanism for the  $\text{CeCu}_2 \rightarrow \text{Fe}_2\text{P}$  transition.

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