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Large hydrogen capacity in hydrides R_2Ni_2In–H (R = La, Ce, Pr, Nd) with new structure type

M. Dzevenko[a,b], K. Miliyanchuk[a,b], Ya. Filinchuk[c], O. Stelmakhovych[b], L. Akselrud[a], L. Havela[b,*], Ya. Kalychak[a]

[a] *Faculty of Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya 6, 79005 Lviv, Ukraine*
[b] *Department of Condensed Matter Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic*
[c] *SNBL at ESRF, BP 220 38043 Grenoble, France*

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ABSTRACT

Several new hydrides with the composition $R_2Ni_2InH_x$ (R = La, Ce, Pr, Nd; $x \approx 4.5$–5.0) were synthesized. They are based on the R_2Ni_2In compounds crystallizing in the Mo_2FeB_2 structure type. So as to accommodate high amount of H atoms (x can theoretically reach the value of 6), the structure changes to orthorhombic, space group *Pbam*, while the unit-cell volume increases by 10–20%. Nd_2Ni_2In was found antiferromagnetic, with a first-order magnetic phase transition at $T_N = 8$ K. Applied magnetic field $\mu_0H < 0.3$ T induces ferromagnetism. T_N of $Nd_2Ni_2InH_{4.5}$, which is a more regular antiferromagnet, is reduced to 5 K.

1. Introduction

R_2T_2In compounds belong to a large family of rare-earth (and also actinide) based compounds, which crystallize with the Mo_2FeB_2 structure type (space group $P4/mbm$) (for overview see Refs. [1,2] and references therein). Their structure type is characterized by bilayers along the shortest lattice parameter c, and consists of trigonal (type AlB_2) and tetragonal (type CsCl) prisms. Such materials have been studied from the point of view of 4f magnetism for R from the group of regular rare earths; anomalous rare earths (Ce, Yb) were studied in terms of valence fluctuations of the 4f elements (as Ce_2Ni_2In and Ce_2Rh_2In [3,4]). Ce_2Cu_2In is characterized by antiferromagnetic order below 5.5 K, whereas for its hydride $Ce_2Cu_2InH_{2.8}$ the fingerprint of magnetic order was lost [5]. The compounds R_2Cu_2In (R = Gd–Tm) exibit ferromagnetic behaviour with $T_C \approx 90$ K or lower [6]. Finally, those including light actinides (mostly U) were investigated with the aim to better understand the peculiarities of the 5f band magnetism, for which the varying type of the nearest-neighbour spacing of the magnetic atoms within one structure type provides a unique opportunity. Another degree of freedom of the Mo_2FeB_2 structure type is offered by the possibility of interstitial doping by hydrogen, which was demonstrated for U_2T_2Sn and U_2T_2In compounds, modifying considerably their magnetic properties [7,8].

In this paper we describe the results of the investigation of hydrogen absorption properties of R_2Ni_2In (R = La, Ce, Pr, Nd) compounds (following a preliminary report in Ref. [9]). We introduce basic properties of this new class of materials, including details of crystal structure of the hydrides.

2. Experimental

R_2T_2In compounds were prepared by arc melting of pure elements (the nominal purity R—99.8 wt.% R, Ni—99.99 wt.% Ni, and In—99.99 wt.% In) under Ar atmosphere. The buttons were melted two times to ensure homogeneity. The total mass of each alloy was about 1 g. The mass losses during melting did not exceed 1%.

The alloys were subsequently crushed in sub-millimeter pieces and heated to $T = 473$ K in vacuum (better than 1×10^{-6} mbar) so as to remove adsorbed impurities. After introducing hydrogen gas, samples started to absorb hydrogen readily. The hydrogenation was carried out at the room temperature and hydrogen pressure 500 mbar. The hydrogen absorption was monitored by the pressure drop in the system. The amount of hydrogen absorbed was recalibrated to ambient temperature, yielding the stoichiometry of the compounds used below.

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* Corresponding author. Tel.: +420 221911351.
E-mail address: havela@mag.mff.cuni.cz (L. Havela).

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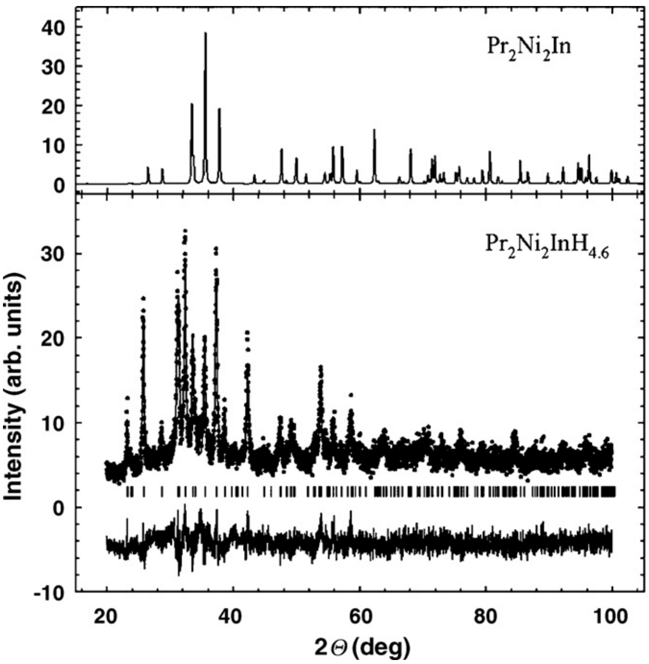

Fig. 1. Theoretical X-ray diffraction pattern of Pr_2Ni_2In (upper panel); observed (♦), calculated (–), and difference X-ray diffraction pattern of $Pr_2Ni_2InH_{4.6}$ hydride.

The crystal structure was investigated by means of X-ray powder diffraction, using the HZG-4a (Cu Kα-radiation) or Seifert XRD7 (Cu $K\alpha_1$-radiation, graphite monochromator) diffractometers. The programs Fullprof [10] and CSD [11] were used for the data analysis.

Pr_2Ni_2In–H was studied by 2D (MAR345 IP) synchrotron powder diffraction at the Swiss-Norwegian Beam Lines (λ = 0.0808136 nm) at ESRF (Grenoble, France). Quantum Design PPMS equipment was used for the magnetic and heat capacity studies of Nd_2Ni_2In and its hydride $Nd_2Ni_2InH_{4.5}$ in the temperature range 2–300 K and magnetic fields up to 9 T (magnetization) or 12 T (heat capacity). In the magnetization study, the grains of the samples were fixed in random orientation by acetone-soluble glue, which prevents any rotation of individual grains under the influence of a magnetic field. The heat capacity was measured on a bulk piece for Nd_2Ni_2In and on a pellet produced by pressing the powder in a die with WC piston faces in the case of the hydride.

3. Results and discussion

3.1. Structure studies

The hydrogenation process as described above led for all R_2Ni_2In (R = La, Ce, Pr, Nd) compounds to a hydrogen absorption corresponding to approximately 4.5 H atoms per formula unit and to structure modifications. The first inspection of X-ray diffraction patterns indicated that the hydrides are isostructural and their structure is different than that of the initial compounds (see Fig. 1 showing the patterns of Pr_2Ni_2In and $Pr_2Ni_2InH_{4.6}$). The finding that we indeed deal with single-phase hydrides was corroborated by the fact that the temperature-induced H desorption, which is completed below about $T = 1273$ K, recovers the original crystal structure. In case the hydrogenation was suspended before the full absorption was achieved, a mixture of the initial compound and the hydride was observed in the X-ray diffraction pattern. This suggests that the hydrides obtained are in fact β-hydrides, separated from the initial structure by a two-phase region.

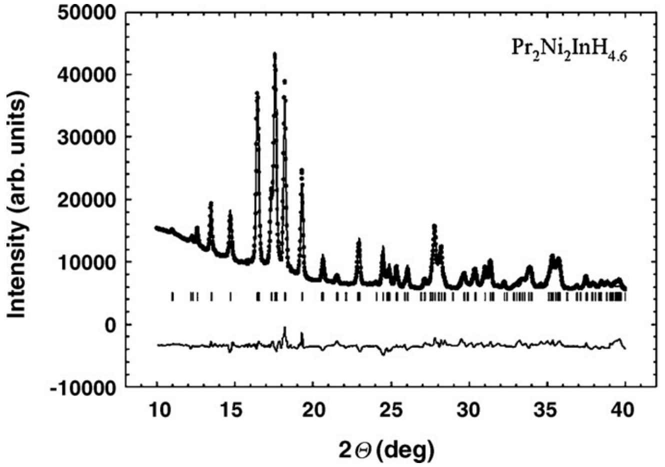

Fig. 2. Observed (♦), calculated (–), and difference synchrotron diffraction pattern of $Pr_2Ni_2InH_{4.6}$ hydride at room temperature (λ = 0.0808136 nm).

A more detailed X-ray diffraction analysis shows that the formation of hydrides leads to an anisotropic expansion of the unit cells in the [1 0 0] direction, with a small compression in the [0 1 0] and [0 0 1] directions. The unit cell volume expansion is quite large, considerably exceeding 10% (see Table 1). As a result of the anisotropic expansion, the symmetry changes from tetragonal to orthorhombic, adopting with the space group *Pbam*. Crystal structure data and details of structure refinement are listed in Table 2. A certain exception is represented by Ce_2Ni_2In, which tends to decompose in the course of the hydrogenation process, forming besides the quaternary hydride $Ce_2Ni_2InH_{4.8}$ also two spurious phases Ce_7Ni_3 (space group $P6_3mc$) and Ce_2Ni_7 (space group $P6_3/mmc$).

The synchrotron-radiation investigation of $Pr_2Ni_2InH_{4.6}$ hydride was performed on the sample sealed into a glass capillary (0.2 mm diameter) using the wavelength λ = 0.808136 Å (Fig. 2). The data obtained confirmed the results of the conventional X-ray diffraction. The lattice parameters obtained are: $a = 0.84366(7)$, $b = 0.75524(6)$, $c = 0.38120(3)$ nm, $V = 0.24289(6)$ nm^3 ($\underline{R}_I = 11.0\%$, $R_P = 16.4\%$). The atomic coordinates and thermal parameters are following: Pr 4*h* *x y* 1/2 ($x = 0.6807(5)$, $y = 0.1700(6)$); Ni 4*g* *x y* 0 ($x = 0.0983(9)$, $y = 0.6468(12)$); In 2*a* 0 0 0; $B_{iso} = 0.0078(7)$ nm^2 for all atoms. The lattice parameters and atomic coordinates are quite different for the samples measured with Cu Kα-radiation and syn-

Table 1
Crystallographic data of R_2Ni_2In (R = La, Ce, Pr, Nd) compounds and their hydrides.

Compound	Space group	*a* (nm)	*b* (nm)	*c* (nm)	$\Delta V/V_0$ (%)
La_2Ni_2In	*P4/mbm*	0.7636(2)	–	0.3906(2)	–
$La_2Ni_2InH_{5.0}$	*Pbam*	0.9079(4)	0.7608(4)	0.3782(3)	14.7
Ce_2Ni_2In	*P4/mbm*	0.7527(2)	–	0.3722(1)	–
$Ce_2Ni_2InH_{4.8}$	*Pbam*	0.8995(4)	0.7549(4)	0.3720(2)	19.5
Pr_2Ni_2In	*P4/mbm*	0.7525(2)	–	0.3819(1)	–
$Pr_2Ni_2InH_{4.6}$	*Pbam*	0.8930(4)	0.7511(3)	0.3712(2)	14.8
$Pr_2Ni_2InH_{4.6-x}$[a]	*Pbam*[a]	0.84366(7)[a]	0.75524(6)[a]	0.38120(3)[a]	12.5[a]
Nd_2Ni_2In	*P4/mbm*	0.7506(2)	–	0.3789(1)	–
$Nd_2Ni_2InH_{4.5}$	*Pbam*	0.8448(5)	0.7505(5)	0.3888(3)	15.5

[a] Synchrotron data.