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Crystal structures of the R_2Ni_2Ga (R = Tb, Dy) hydrides and tuning of the hydrogenation properties by *p*-element substitution

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Intermetallics with the structure type W_2CoB_2 (Pearson symbol *oI*10, space group *Immm*) are promising materials for hydrogen storage. The present work reports on hydrogenation of the W_2CoB_2-type intermetallics Tb_2Ni_2Ga and $Dy_2Ni_2Ga_{1-x}Al_x$ (x = 0, 0.2, 0.5, 0.8, 1). The hydrides were synthesized at room temperature and hydrogen pressures below ambient ($p(H_2)$ = 0.4-0.5 bar). Hydrogenation led to substantial lattice expansion, reaching $\Delta V/V$ = 18.4% for Tb_2Ni_2Ga, and increasing from 18.5% to 22.5% with increasing Al content within the $Dy_2Ni_2Ga_{1-x}Al_x$ series. The change in the lattice is highly anisotropic: the increase of the lattice parameters *b* and *c* is accompanied by a decrease of the lattice parameter *a*. Based on an analysis of the free space in the metal matrix of $Tb_2Ni_2GaH_{5.1}$, a model for the crystal structure is proposed with two hydrogen sites inside tetrahedra [Tb_3Ni] and [Tb_2Ni_2], yielding a theoretical composition of $Tb_2Ni_2GaH_6$ for the hydride. Limited substitution of Ga for Al improved the hydrogenation properties of the R_2Ni_2Ga compounds, leading to faster hydrogenation kinetics and higher hydrogen content.

Intermetallic / Hydride / X-ray diffraction / Crystal structure

Introduction

The change from consuming fossils, *i.e.* coal, oil and natural gas, to renewable energy sources is crucial to reduce the level of greenhouse gases. Meantime, the overall energy demand is increasing worldwide due to population growth, urbanization, industrialization, *etc*. Hence, development of alternative energy carriers is vital to establish a sustainable society. Hydrogen might be a solution to the above-mentioned problems, because it fits energy carrier criteria and is both available and eco-friendly [1,2]. Hydrogen storage methods can be classified as physical (compressed gas, liquefied hydrogen) or chemical (metal hydrides, borohydrides, organic compounds, *etc.*) [3-5]. The metal hydrides are promising solid-state hydrogen storage materials thanks to their high hydrogen capacity, high volumetric hydrogen density, reversible cycling, safety, and tunable properties achieved *via* compositional and/or structural design.

R_2T_2M (R = *f*-metal, T = *d*-metal, M = *p*-element) intermetallics with W_2CoB_2-type structure (Pearson symbol *oI*10, space group *Immm*) exhibit promising hydrogen-sorption properties, as they can absorb up to 6 H atoms per formula unit even at room temperature and hydrogen pressures below 1 bar. The rate of hydrogenation strongly depends on the nature of the *p*-element. The Al-containing representatives (Gd_2Ni_2Al, Er_2Ni_2Al, Lu_2Ni_2Al) absorb hydrogen within seconds, whereas the Sn-counterparts (Gd_2Ni_2Sn, Tb_2Ni_2Sn) absorb hydrogen within several hours [6]. More recently, the hydrogenation of Ga-based representatives (Tb_2Co_2Ga and Tb_2Ni_2Ga) was studied, and they were found to absorb hydrogen within minutes [7]. For Tb_2Co_2Ga the W_2CoB_2-type metal matrix was preserved after hydrogenation, however, a full crystal structure determination of the Tb_2Ni_2Ga hydride was not possible due to non-negligible reduction of the grain size upon hydrogenation, or even partial amorphization of the sample, reflected in pronounced peak broadening.

Both Dy_2Ni_2Ga and Dy_2Ni_2Al (W_2CoB_2 structure type) are known from the literature [8,9]. Considering that the hydrogenation properties of the W_2CoB_2-type intermetallics depend on the nature of the *p*-element and the extremely high reactivity of the aluminides, the possibility of substituting Ga for Al paves the way for fine-tuning of the hydrogenation properties of R_2Ni_2Ga. In this work, the results of refinements of the metal matrix of the R_2Ni_2Ga (R = Tb, Dy) hydrides and the effect of elemental substitution on the crystal structure and hydrogenation properties of Dy_2Ni_2Ga are reported.

Experimental details

Alloys with compositions Tb_2Ni_2Ga and $Dy_2Ni_2Ga_{1-x}Al_x$ (x = 0, 0.2, 0.5, 0.8, 1) were synthesized by arc-melting the constituent metals (at least 99.9 % purity). The metal pieces were arc-melted in argon atmosphere on a water-cooled copper hearth. The lumps were returned and remelted once to ensure homogeneity. The resulting alloys were annealed at 873 K in sealed evacuated quartz ampoules for two (Tb_2Ni_2Ga) or four ($Dy_2Ni_2Ga_{1-x}Al_x$) months, and then quenched. The phase composition was checked by X-ray powder diffraction (DRON-2.0M diffractometer, Fe *K*α radiation).

Hydrogenation of the intermetallics was conducted on alloys crushed to submillimeter-sized particles. The surface of the samples was activated by heating up to 250°C over 2 h in oil-free vacuum ($p < 1 \cdot 10^{-5}$ mbar), in order to desorb surface contaminants. After the activation, hydrogen gas was introduced into the reaction chamber. The hydrogenation reaction was conducted at room temperature and hydrogen pressures of 0.3-0.5 bar. The amount of absorbed hydrogen was estimated volumetrically by monitoring the pressure drop in the reaction chamber.

The crystal structures of the intermetallics and their respective hydrides were determined by X-ray powder diffraction (Bruker diffractometer, Cu *K*α radiation) performing Rietveld refinements, using FullProf software [10]. The program DIAMOND [11] was used to visualize the crystal structure and the coordination polyhedra. The structural cavities were calculated and visualized using MoloVol [12] and ChimeraX [13] programs, respectively.

Results

Hydrogenation of Tb_2Ni_2Ga and Dy_2Ni_2Ga

The phase analysis by X-ray diffraction of the alloys Tb_2Ni_2Ga and Dy_2Ni_2Ga confirmed the formation of the W_2CoB_2-type phases; no additional phases were detected. The cell parameters of the compounds agree with those reported in the literature (Table 1). The hydrogenation of Tb_2Ni_2Ga and Dy_2Ni_2Ga was conducted at room temperature and hydrogen pressures of 530 and 387 mbar, respectively, resulting in the formation of the hydrides $Tb_2Ni_2GaH_{5.1}$ and $Dy_2Ni_2GaH_{4.5}$ (Fig. 1). The hydrides were in the form of fine powders.

Table 1 Cell parameters, relative cell changes, atomic coordinates of the metal atoms, overall displacement parameters for Tb_2Ni_2Ga and Dy_2Ni_2Ga, before and after hydrogenation.

Atom	Wyckoff position	*x*	*y*	*z*
Tb_2Ni_2Ga, space group *Immm*, a = 4.1839(3) Å, b = 5.3718(4) Å, c = 8.3088(6) Å, V = 186.74(2) Å^3, $B_{ov.}$ = 0.83(8) Å^2				
Tb	4*j*	½	0	0.2967(5)
Ni	4*h*	0	0.232(2)	½
Ga	2*a*	0	0	0
$Tb_2Ni_2GaH_{5.1}$, space group *Immm*, a = 3.736(4) Å, b = 6.505(9) Å, c = 9.093(5) Å, V = 221.0(4) Å^3, $B_{ov.}$ = 0.99(7) Å^2, $\Delta a/a$ = -10.7%, $\Delta b/b$ = 21.1%, $\Delta c/c$ = 9.4%, $\Delta V/V$ = 18.4%				
Tb	4*j*	½	0	0.2912(7)
Ni	4*h*	0	0.295(2)	½
Ga	2*a*	0	0	0
Dy_2Ni_2Ga, space group *Immm*, a = 4.1744(2) Å, b = 5.3499(3) Å, c = 8.2618(4) Å, V = 184.51(2) Å^3, $B_{ov.}$ = 0.74(8) Å^2				
Dy	4*j*	½	0	0.2991(3)
Ni	4*h*	0	0.2405(12)	½
Ga	2*a*	0	0	0
$Dy_2Ni_2GaH_{4.5}$, space group *Immm*, a = 3.734(2) Å, b = 6.468(3) Å, c = 9.055(3) Å, V = 218.7(2) Å^3, $B_{ov.}$ = 1.8(5) Å^2, $\Delta a/a$ = -10.6%, $\Delta b/b$ = 20.9%, $\Delta c/c$ = 9.6%, $\Delta V/V$ = 18.5%				
Dy	4*j*	½	0	0.2852(3)
Ni	4*h*	0	0.2778(11)	½
Ga	2*a*	0	0	0

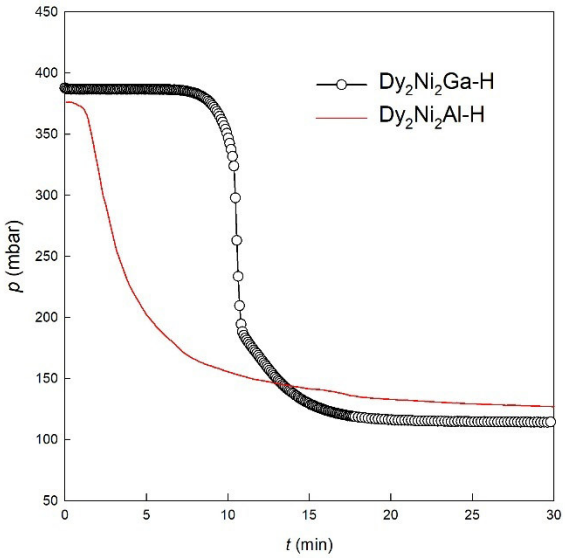


Fig. 1 Hydrogenation curves for Dy_2Ni_2Ga (m = 320.2 mg) and Dy_2Ni_2Al (m = 232.3 mg) (V_{system} = 163.1 cm^3).

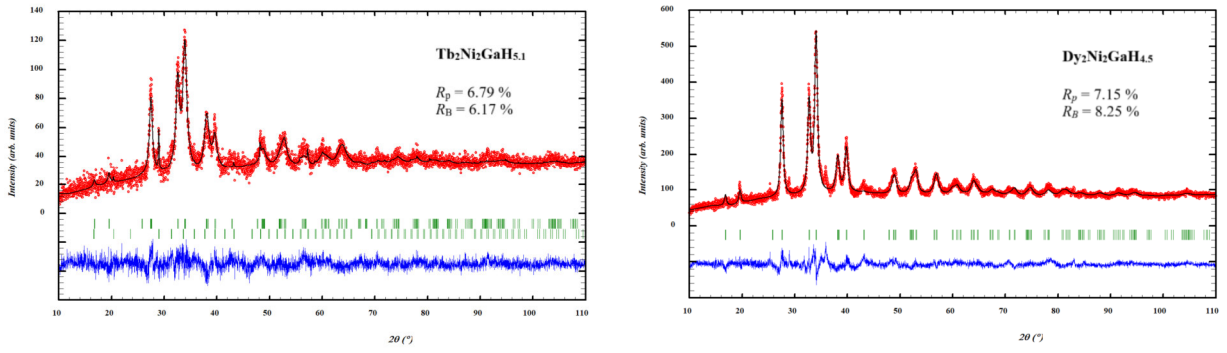
The impact of hydrogenation on the crystal structure of the intermetallics was studied by X-ray powder diffraction. The X-ray diffraction patterns were well described by a W_2CoB_2-type model (Fig. 2). A small amount (~2.9(3) wt.%) of oxide impurity Tb_2O_3 (space group Ia-3, a = 10.669(4) Å) was identified for $Tb_2Ni_2GaH_{5.1}$. The modifications of the crystal lattice for Tb_2Ni_2Ga and Dy_2Ni_2Ga after hydrogenation (see Table 1) indicate comparable hydrogenation behavior: the lattice is expanded along the b- and c-axis ($\Delta b/b$ = 21.1% and 20.9%, respectively), and the expansion is accompanied by lattice shrinkage along the a-axis. The volume increase reached $\Delta V/V$ = 18.4% and 18.5% for Tb_2Ni_2Ga and Dy_2Ni_2Ga, respectively. While the hydrogenation timescales are similar (induction time ~10 min), the Tb-containing compound absorbed slightly more hydrogen atoms per formula unit, 5.1 H/f.u. *vs* 4.5 H/f.u., which is consistent with the larger atomic size of Tb compared to Dy.

The atomic arrangement of the metal matrix is preserved after hydrogenation. The hydrogenation affects the position of the Ni atoms (y(Ni) < ¼ for the intermetallics and y(Ni) > ¼ for the hydrides), which consequently brings them closer to the Ga atoms. This shift leads to changes in the structure-forming blocks: trigonal prisms Ni[R_4Ga_2] (R = Tb or Dy) in the intermetallics and Ga[Ni_4] squares in the hydrides (Fig. 3). As a result of the abovementioned structural changes, and the modification of the lattice parameter ratio a/b (intermetallic) > a/b (hydride), the crystal structures of the hydrides can be assigned the structure type K_2PtS_2, which is isopointal to the initial W_2CoB_2-type [14].

Effect of Al-substitution on the hydrogenation properties of Dy_2Ni_2Ga

The phase analysis by X-ray diffraction confirmed the existence of a continuous solid solution between Dy_2Ni_2Ga and Dy_2Ni_2Al. The cell volume linearly increased with increasing Al content, as expected from the difference in atomic radii between Ga and Al (Fig. 4). The increase of the cell volume is caused by expansion in the direction of the b- and c-axis, while the lattice parameter a (corresponding to the height of the structure-forming trigonal prisms) decreases, even if not significantly (Table 2).

The hydrides of the $Dy_2Ni_2Ga_{1-x}Al_x$ intermetallics were synthesized at room temperature and hydrogen pressures of 415, 401, 382, and 377 mbar for $Dy_2Ni_2Ga_{0.8}Al_{0.2}$, $Dy_2Ni_2Ga_{0.5}Al_{0.5}$, $Dy_2Ni_2Ga_{0.2}Al_{0.8}$, and Dy_2Ni_2Al, respectively. The reaction started after a short induction period of 4, 1.5, 0.8, and 0.8 minutes, respectively. Fig. 1 represents the difference in the hydrogenation kinetics between Dy_2Ni_2Ga and Dy_2Ni_2Al. The hydrogen content in the hydride does not depend significantly on the composition of the intermetallic within the solid solution (see Table 2).



a *b*

Fig. 2 Observed, calculated and difference X-ray diffraction patterns for $Tb_2Ni_2GaH_{5.1}$ (*a*) and $Dy_2Ni_2GaH_{4.5}$ (*b*) (Cu $K\alpha$ radiation), profile and Bragg reliability factors.

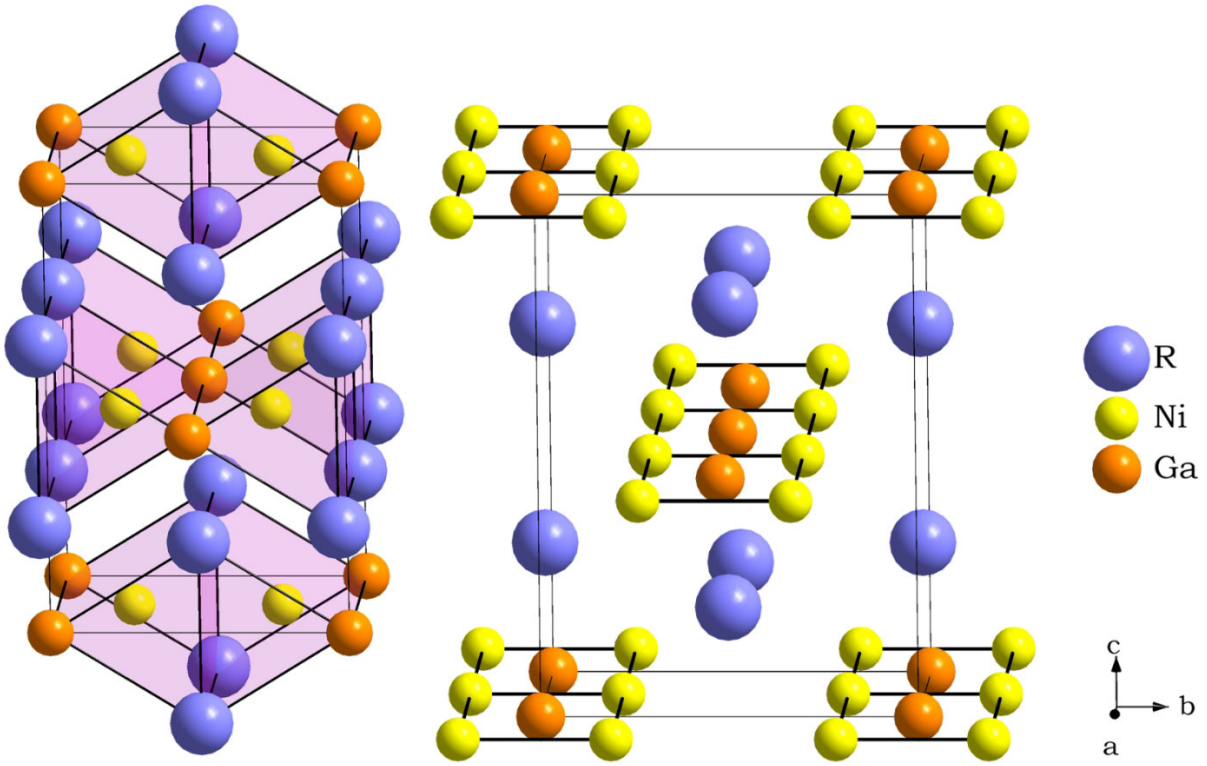


Fig. 3 Arrangement of layers of trigonal prisms (*a*) and ribbons of squares (*b*) in R_2Ni_2Ga (R = Tb or Dy) before and after hydrogenation, respectively.

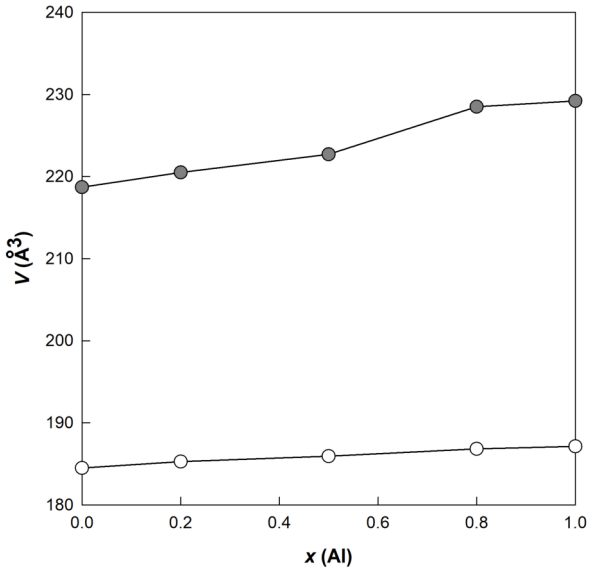


Fig. 4 Dependence of the cell volume on the composition of $Dy_2Ni_2Ga_{1-x}Al_x$ (open circles) and the corresponding hydrides (filled circles).

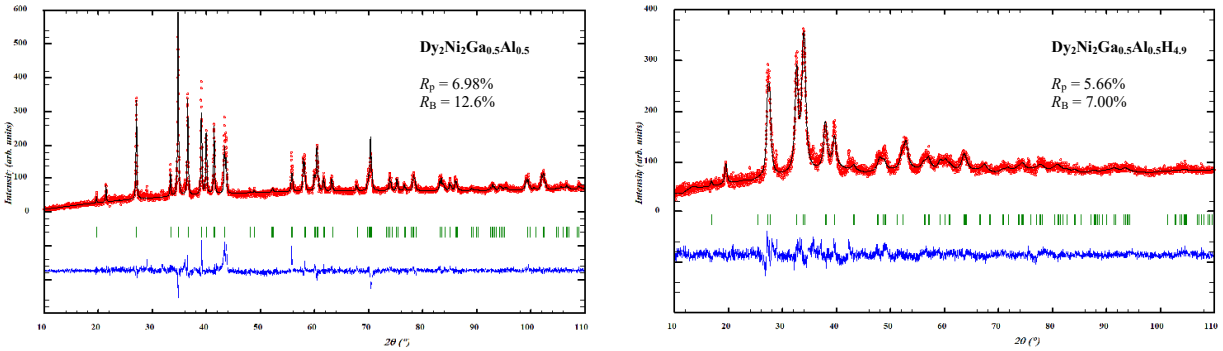
The X-ray powder diffraction patterns of the hydrides were well described applying the W_2CoB_2-type model (Fig. 5). The significant peak broadening in the X-ray patterns of the hydrogenated samples prevented a complete structure refinement. The lattice parameters of the hydrides are given in Table 2. The dependence of the cell volume of the hydrides on the composition of the $Dy_2Ni_2Ga_{1-x}Al_x$ metal matrix exhibits a discontinuity at x(Al) ≈ 0.5 (see Fig. 4), which can be a sign of a different influence of hydrogenation on the samples in the Ga-rich and Al-rich regions, *e.g.* different hydrogen positions or additional lattice distortion.

Discussion

Up to now, only models, based on an analysis of the modifications of the metal matrix upon hydrogenation, have been proposed for the crystal structures of hydrides of intermetallics with the structure type W_2CoB_2. Due to the small scattering cross-section of hydrogen atoms for X-rays, the structure could not be solved directly from the X-ray diffraction data.

Table 2 Cell parameters (a, b, c, V) of $Dy_2Ni_2Ga_{1-x}Al_x$ (x = 0.2, 0.5, 0.8, 1) phases and their hydrides, and relative change of the lattice parameters after hydrogenation ($\Delta a/a$, $\Delta b/b$, $\Delta c/c$, $\Delta V/V$).

Compound	a (Å)	b (Å)	c (Å)	V (Å)	$\Delta a/a$ (%)	$\Delta b/b$ (%)	$\Delta c/c$ (%)	$\Delta V/V$ (%)
Dy_2Ni_2Ga	4.1744(2)	5.3499(3)	8.2618(4)	184.51(2)	–	–	–	–
$Dy_2Ni_2GaH_{4.5}$	3.734(2)	6.468(3)	9.055(3)	218.7(2)	-10.6	20.9	9.6	18.5
$Dy_2Ni_2Ga_{0.8}Al_{0.2}$	4.1758(4)	5.3609(5)	8.2773(7)	185.29(3)	–	–	–	–
$Dy_2Ni_2Ga_{0.8}Al_{0.2}H_{5.0}$	3.748(3)	6.478(4)	9.079(4)	220.5(2)	-10.2	20.8	9.7	19.0
$Dy_2Ni_2Ga_{0.5}Al_{0.5}$	4.1737(3)	5.3721(4)	8.2933(6)	185.95(2)	–	–	–	–
$Dy_2Ni_2Ga_{0.5}Al_{0.5}H_{4.9}$	3.790(2)	6.459(3)	9.098(4)	222.7(2)	-9.2	20.2	9.7	19.8
$Dy_2Ni_2Ga_{0.2}Al_{0.8}$	4.1725(2)	5.3852(3)	8.3148(4)	186.84(2)	–	–	–	–
$Dy_2Ni_2Ga_{0.2}Al_{0.8}H_{5.2}$	3.864(2)	6.427(3)	9.202(4)	228.5(2)	-7.4	19.3	10.7	22.3
Dy_2Ni_2Al	4.1699(3)	5.3913(4)	8.3246(5)	187.14(2)	–	–	–	–
$Dy_2Ni_2AlH_{5.2}$	3.881(2)	6.400(3)	9.229(4)	229.2(2)	-6.9	18.7	10.9	22.5



a *b*

Fig. 5 Observed, calculated and difference X-ray diffraction patterns for $Dy_2Ni_2Ga_{0.5}Al_{0.5}$ (*a*) and $Dy_2Ni_2Ga_{0.5}Al_{0.5}H_{4.9}$ (*b*) (Cu *K*α radiation).

In this work, we applied a different approach in the crystal chemical analysis of the metal hydrides by identifying the voids in the metal matrix of the hydride. We performed such an analysis for $Tb_2Ni_2GaH_{5.1}$, applying the program MoloVol [12], the algorithm of which is based on "rolling" an imaginary spherical probe through the structure, while recording the position of the probe's center and its outer boundary. We defined the radii of the metal atoms (r_{Tb} = 1.77 Å, r_{Ni} = 1.24 Å, r_{Ga} = 1.22 Å) and the probe atom (r_H = 0.4 Å). Thereby, a map of voids suitable for hydrogen was generated (grid resolution 0.04 Å, optimization depth 4). The calculated cavities occupy ~25% of the cell volume and form interconnected channels throughout the structure (Fig. 6), which are potential pathways for hydrogen migration and intercalation. Amongst the cavities, two non-equivalent voids suitable for occupation by hydrogen atoms were further analyzed. One of them corresponds to a tetrahedral site H1[Tb_3Ni] in Wyckoff position 8*l* of space group *Immm*, whereas the second one corresponds to an octahedral site H2[Tb_4Ni_2] in 2*c* (Fig. 7). Given the large size of the octahedral site H2, two related tetrahedral sites, H2A[Tb_2Ni_2] and H2B[Tb_2Ni_2], in Wyckoff position 4*f* (2×2 tetrahedral positions per octahedron), may be considered. Neighboring tetrahedra H2A and H2B share a common face, so that only one of them can be occupied by hydrogen atoms. Based on the results, a crystal structure model of $Tb_2Ni_2GaH_{5.1}$, where hydrogen atoms are located in H1[Tb_3Ni] (8*l* site) and H2B[Tb_2Ni_2] (4*f* site) tetrahedra, is proposed. This model agrees with the ones previously proposed for $Er_2Ni_2AlH_{5.3}$ and $Tb_2Co_2GaH_{6.2}$ based on an analysis of the crystal structure of the metal matrix [6,7], and yields a theoretical hydrogen content of 6 H/f.u.

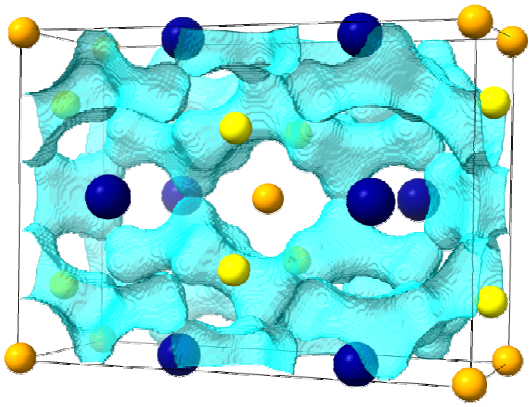


Fig. 6 Map of interconnected cavities large enough for hydrogen to diffuse through the metal matrix of $Tb_2Ni_2GaH_{5.1}$ (Tb atoms blue, Ni yellow, Ga orange).

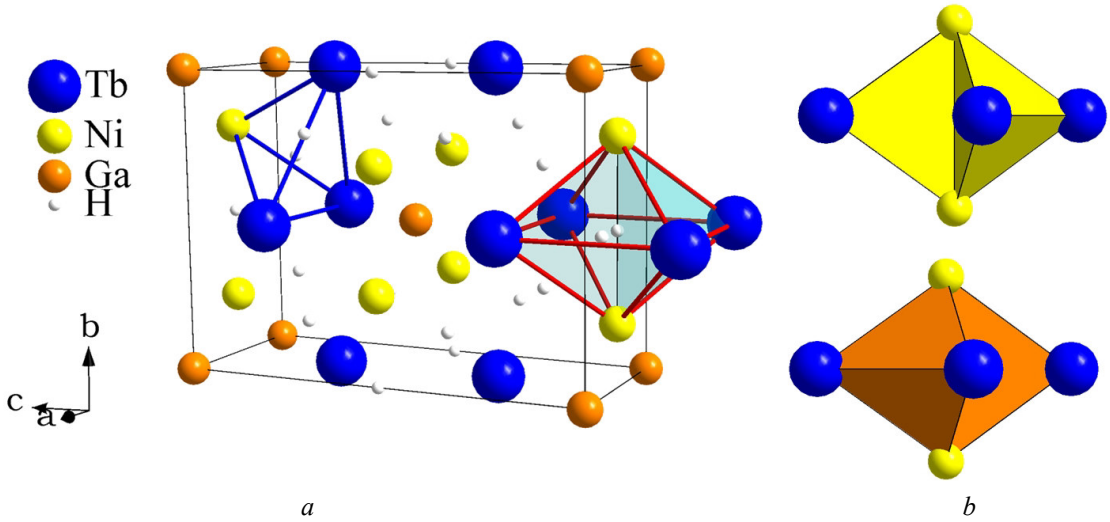


Fig. 7 Crystal structure model for the hydride $Tb_2Ni_2GaH_{5.1}$ with sites H1 and H2B (*a*); the octahedral site H2 is split into two tetrahedral ones (*b*): H2A (*top*) and H2B (*bottom*).

The substitution of Al for Ga in R_2Ni_2Ga leads to faster hydrogenation kinetics, however, in the Al-rich region amorphization of the samples after hydrogenation is significant and further lattice deformation is not excluded. Hence, limited substitution of Al for Ga favors the hydrogenation properties, while additional substitution results in different mechanisms of lattice modification and amorphization.

Conclusions

This work is part of a systematic study of W_2CoB_2-type intermetallics in *R–T–M* systems as hydrogen-sorption materials. The intermetallics Tb_2Ni_2Ga and $Dy_2Ni_2Ga_{1-x}Al_x$ easily absorbed hydrogen at room temperature and relatively low hydrogen pressures. The presence of interconnected cavities within the W_2CoB_2-type framework is favorable for the hydrogenation process. Limited substitution of Al for Ga improved the hydrogenation properties of the intermetallics, leading to faster hydrogenation kinetics and higher hydrogen content.

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References

[1] K.T. Møller, T.R. Jensen, E. Akiba, H. Li, *Prog. Nat. Sci.: Mater. Int.* 27 (2017) 34-40.

[2] S. Sharma, S. Agarwal, A. Jain, *Energies* 14 (2021) 7389 1-28.

[3] B. Doğan. *Proceedings of the ASME 2006 Pressure Vessels and Piping/ICPVT-11 Conference. Volume 6: Materials and Fabrication* (2006) 571-578.

[4] M.V. Lototskyy, V.A. Yartys, B.G. Pollet, R.C. Bowman Jr., *Int. J. Hydrogen Energy* 39 (2014) 5818-5851.

[5] N. Klopčič, I. Grimmer, F. Winkler, M. Sartory, A. Trattner, *J. Energy Storage* 72 (2023) 108456.

[6] K. Miliyanchuk, L. Havela, Y. Tsaruk, S. Maskova, R. Gladyshevskii, *J. Alloys Compd.* 25 (2015) 911-916.

[7] K. Miliyanchuk, S. Maskova-Cerna, L. Havela, N. Saidov, Y. Tokaychuk, M. Dopita, R. Gladyshevskii, *J. Solid State Chem.* 296 (2021) 121978 1-12.

[8] V.A. Romaka, Y. Grin, Y.P. Yarmoluyk, O.S. Zarechnyuk, R.V. Skolozdra, *Phys. Met. Metallogr.* 54 (1982) 58-64.

[9] R.M. Rykhal', O.S. Zarechnyuk. V.M. Mandzin, *Dopov. Akad. Nauk Ukr. RSR, Ser. A* (1980) (6), 77-79

[10] J. Rodriguez-Carvajal, Recent developments of the program FULLPROF, Commission on Powder Diffraction (IUCr), *Newsletter* 26 (2001) 12-19.

[11] DIAMOND v2.1, Crystal Impact GbR, Bonn, Germany, 1996-1999.

[12] J.B. Maglic, R. Lavendomme, *J. Appl. Crystallogr.* 55 (2022) 1033-1044.

[13] E.F. Pettersen, T.D. Goddard, C.C. Huang, E.C. Meng, G.C. Couch, T.I. Croll, J.H. Morris, T.E. Ferrin, *Protein Sci.* 30 (2021) 70-82.

[14] W. Bronger, O. Gunter, *J. Less-Common Met.* 27 (1972) 73-79.