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An interrelation of RH_x coordination and H ordering in the structures of intermetallic hydrides

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Abstract

The hydrogen sublattice in the structures of intermetallic hydrides is considered as built from RH_x polyhedra formed by H around R atoms. This approach allowed to describe successfully an interrelation between different structures formed on the basis of isostructural intermetallics and to rationalise the occurring order–disorder transitions. A detailed analysis has been performed for the RT_2H_x hydrides formed by $MgCu_2$-type intermetallic compounds. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Intermetallic hydrides; Crystal structure; Hydrogen ordering; $MgCu_2$ structure type

1. Introduction

Structural phase transitions in the metal and intermetallic hydrides are usually associated with hydrogen ordering in the crystal lattice. The order–disorder transitions proceed at low temperatures and are caused by 'freezing' of hydrogen diffusion between the neighbouring interstices through their common face, with a jump length of approximately 1.2–1.4 Å. Thus, the shortest values of H···H distances in the structures of metal hydrides represent the separations between the next neighbouring interstitial sites, generally located at >2.0 Å. Recent finding of a new type of intermetallic hydrides, $R_3Ni_3In_3D_4$ (R=La,Ce,Nd) [1] showed that the 'rule of 2 Å' is not absolute. D···D pairs with extremely short interatomic distances ranging from 1.570 (Nd) to 1.635 Å (La) are formed in the $R_3Ni_3In_3D_4$ structures, with a nearly complete filling of two R_3Ni sites sharing a common R_3 face.

Two complementary crystal chemical approaches have been used so far to describe the structures of ternary metal hydrides, including (a) their presentation as insertion type compounds, with specific interstitial positions filled by H [2–4] and (b) consideration of the $R_nT_mH_q$ (R, hydride forming metal; T, transition metal) hydrides as consisting of the hydride complexes of transition metal, hydride anions and cations of the hydride-forming metal R [5].

In intermetallic hydrides the sites with the highest amount of R atoms in their surrounding are preferably filled by H atoms [2–4]. R–H bonds are significantly stronger compared to the T–H and X–H (X=non transition element) interactions [6]. This gives a sufficient chemical background to propose a description of the $R_nT_mX_pH_q$ structures as a stacking of polyhedra formed by H atoms (or H sites in hydrides with disordered hydrogen sublattice) around the R atoms. In the present work we will analyse the stacking of the RH_x polyhedra in a particular type of ternary hydrides in order (a) to build the hydrogen sublattice and (b) to rationalise the interrelations between different 'ordered' and 'disordered' structures with the same type of metal sublattice. The crystal chemical analysis will be performed for the known structures of intermetallic hydrides with the filled $MgCu_2$-type structure and $H/RT_2 > 3$ (Table 1). Despite extensive experimental data for these types of hydrides are available, no unified approach to describe interrelation between them has been proposed so far.

Since D-substituted compounds have been used in the experimental studies reported in the original publications on the crystal structures of intermetallic hydrides and no significant chemical and crystal chemical differences appear between the hydrides $R_nT_mX_pH_q$ and corresponding deuterides $R_nT_mX_pD_q$, the symbols H and D and terms 'hydrogen sublattice' and 'deuterium sublattice' are used in the paper as equivalent to each other.

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Table 1
Crystal structure data for the selected intermetallic hydrides with filled $MgCu_2$-type structures

	Deuteride	Space group	Lattice parameters (Å)	Atomic coordinates	Refs.
1	$ZrTi_2D_4$	$Fd\bar{3}m$ (No. 227)	a=8.19	Zr in 8a: 0 0 0 Ti in 16d: 5/8 5/8 5/8 D in 32e: 0.387 x x; n=1	[10]
2	$CeRu_2D_5$	$Fd\bar{3}m$ (No. 227)	a=8.383	Ce in 8a: 0 0 0 Ru in 16d: 5/8 5/8 5/8; n=0.93 D in 96g: 0.190 x 0.006; n=0.44	[8]
3	$ZrV_2D_{4.5}$	$Fd\bar{3}m$ (No. 227)	a=7.913	Zr in 8a: 0 0 0 V in 16d: 5/8 5/8 5/8 D1 in 8b: 1/2 1/2 1/2; n=0.01 D2 in 32e: 0.3989 x x; n=0.39 D3 in 96g: 0.1859 x 0.9993; n=0.25	[11]
4	HfV_2D_4 (77 K)	$I4_1/a$ (No. 88)	a=5.42; c=7.75	Hf in 4a: 0 1/4 1/8; V in 8d: 0 0 1/2 D in 16f: 0.182; −0.068; 0.060; n=1	[12]
5	$LaMg_2D_7$ (295 K)	$P4_12_12$ (No. 92)	a=6.3900; c=9.5782	La in 4a: 0.2683 x 0 Mg in 8b: 0.0258 0.2618 0.3519 D1 in 8b: 0.0319 0.0320 0.1294; n=1 D2 in 8b: 0.0709 0.4332 0.1809; n=1 D3 in 8b: 0.3052 0.1611 0.2542; n=1 D4 in 4a: 0.7585 x 0; n=1	[7]
6	$ZrCr_2D_{3.8}$ (1.6 K)	$C2/c$ (No. 15)	a=9.3816; b=5.4445; c=9.3495; β=108.946°	Zr in 8f: 0.4361 0.2541 0.0621 Cr1 in 8f: 0.2490 0.0191 0.2505 Cr2 in 4e: 0 0.2467 1/4 Cr3 in 4d: 1/4 1/4 1/2 D1 in 8f: 0.0643 0.1308 0.4327; n=0.848 D2 in 8f: 0.0683 0.4385 0.1297; n=1 D3 in 8f: 0.2534 0.0545 0.0629; n=0.912 D4 in 8f: 0.3753 0.2775 0.2547; n=1	[13]
7	$YMn_2D_{4.3}$ (300 K)	$R3m$ (No. 160)	a=5.571; α=60.846°	Y1 in 1a: 0.1240 x x Y2 in 1a: −0.1240 x x Mn1 in 1a: 0.4927 x x Mn2 in 3b: 0.4945 x 0.0033 D1 in 3b: 0.1247 x 0.5042; n=0.94 D2 in 3b: −0.1422 x 0.2867; n=0.94 D3 in 6c: −0.299 0.144 0.515; n=0.5	[14]
8	$YFe_2D_{3.5}$ (350 K)	$R\bar{3}m$ (No. 166)	a=5.5399; c=13.568.	Y in 6c: 0 0 0.1256 Fe1 in 3b: 0 0 1/2 Fe2 in 9c: 1/2 0 0 D1 in 18h: 0.8610 2x 0.2584; n=0.45 D2 in 36i: 0.233 0.318 0.4426; n=0.37	[15]

2. Results and discussion

Intermetallic hydrides with filled C15 ($MgCu_2$-type) Laves phase structure represent one of the most thoroughly studied group of hydrides with a vast number of representatives covering a wide range of H/RT_2 ratios up to 7 atoms H per formula unit (at. H/f.u.) [3,4,7].

Three types of tetrahedral interstices (8b T_4, 32e RT_3 and 96g R_2T_2) exist in the $MgCu_2$-type structure [4]. Complete filling of 8b and 32e sites by hydrogen atoms is possible from stereochemical considerations and would lead to the formation of stoichiometric hydrides RT_2H and RT_2H_4, respectively.

In contrast, R_2T_2 96g site can only be partially occupied because of short separations of the neighbouring sites each from other. The highest experimentally observed occupancy, n=0.44, was found for $CeRu_2D_{5.28}$ [8]. Analysis of the available crystal structure data for the RT_2H_x hydrides [3,4] shows that R_2T_2 sites are preferentially filled by hydrogen atoms, particularly at low concentrations of H in metallic matrix [9]. Such preference in filling of the R_2T_2 sites is associated with higher content of R in their surrounding and bigger size compared to the other interstices.

For the high hydrogen concentrations exceeding RT_2H_3, which are considered in this paper, the following three

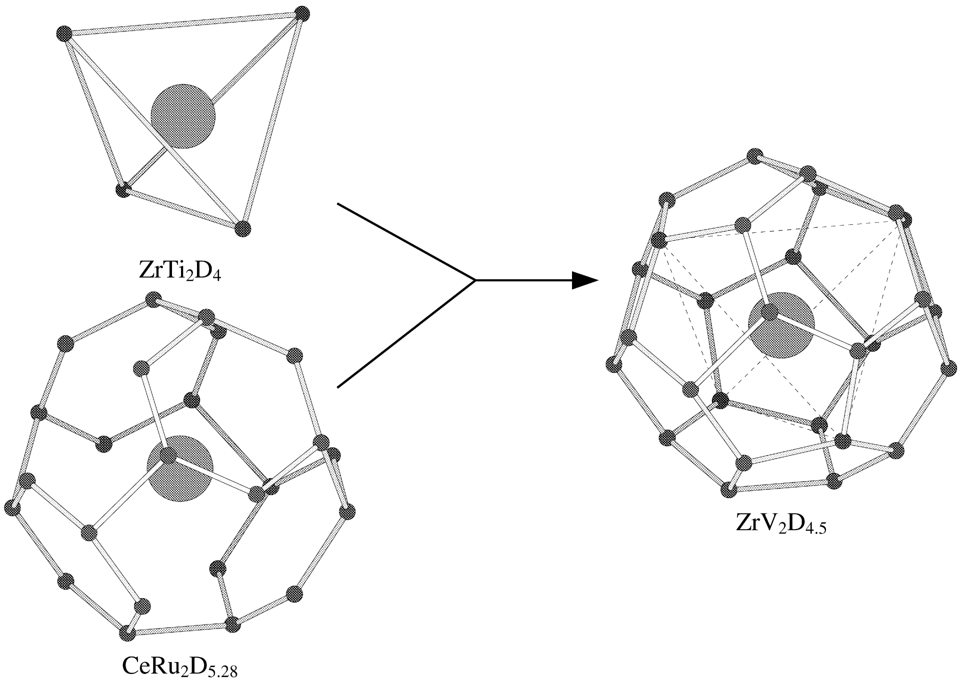

Fig. 1. Coordination of R by D in different $MgCu_2$-type intermetallic hydrides. $ZrTi_2D_4$:ZrD_4 tetrahedron; $CeRu_2D_{5.28}$:CeD_{24} polyhedron; $ZrV_2D_{4.5}$:ZrD_{28} polyhedron.

types of hydrogen distribution are typical:

- (I) 32*e* sites are completely filled ($ZrTi_3$ sites in $ZrTi_2D_4$ [10]);
- (II) 96*g* sites are partially filled (Ce_2Ru_2 sites in $CeRu_2D_{5.28}$ [8]);
- (III) both 96*g* (Zr_2V_2) and 32*e* (ZrV_3) sites are partially filled ($ZrV_2D_{4.5}$ [11]).

Below we will consider the coordination of R atoms by the occupied H sites and will describe the hydrogen sublattice as a spatial stacking of the formed RH_x polyhedra.

In the structure of $ZrTi_2D_4$ hydrogen atoms form non-connected ZrD_4 tetrahedra around Zr atoms (Fig. 1). Hydrogen sublattice can be built from these tetrahedra and

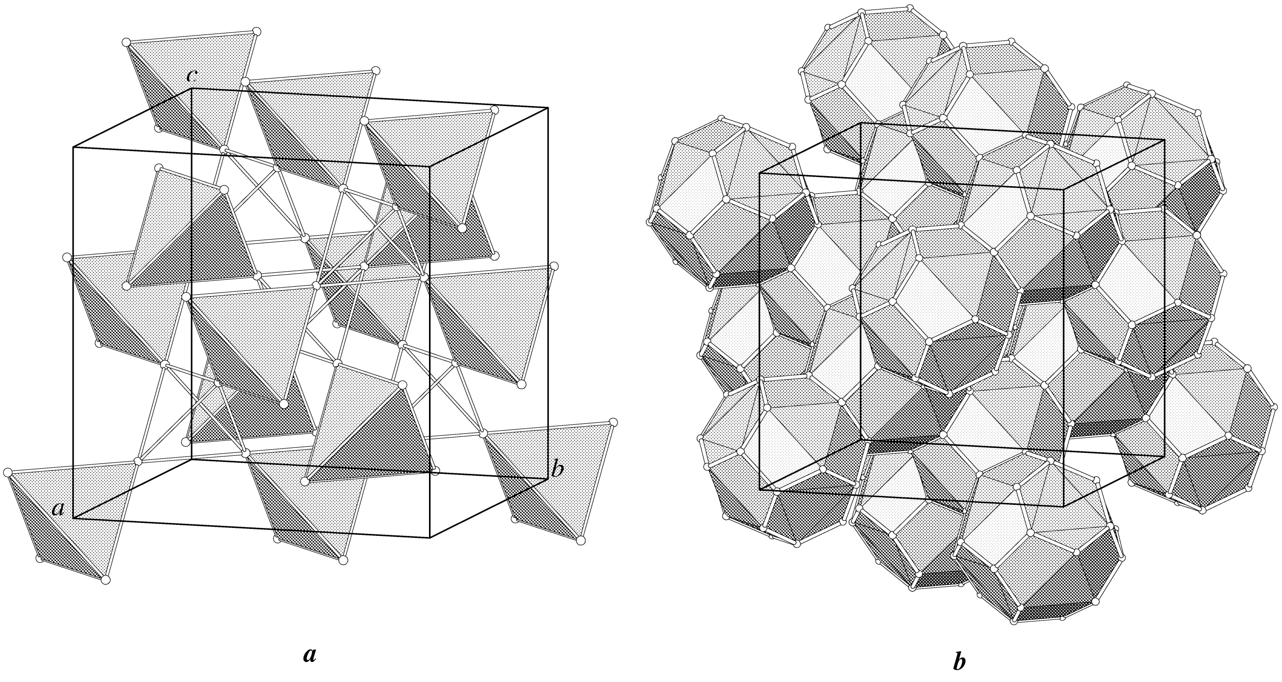

Fig. 2. Stacking of ZrD_4 and D_4 empty tetrahedra in the structure of cubic $ZrTi_2D_4$ (a) and CeD_{24} polyhedra in the structure of cubic $CeRu_2D_{5.28}$ (b).

the equal number of empty D_4 tetrahedra which form a framework in the structure (Fig. 2a).

The 96*g* H(D)-sites form a 24-vertex polyhedron around atom R (Fig. 1). This polyhedron can be considered as consisting of four equal hexagons each oriented perpendicularly to the 3-fold axis (diagonal of the cubic unit cell). Occupation by H (D) atom of a particular position in this polyhedron blocks simultaneous filling of three neighbouring sites. Two of them are located in the same hexagon and one site is positioned in the neighbouring hexagon. As a result, only each second position can be filled by H. Formation of the spatial hydrogen sublattice from the RD_{24} polyhedra proceeds through sharing of common hexagonal faces between the neighbouring polyhedra (Fig. 2b).

Simultaneous occupation of 32*e* and 96*g* sites proceeds in the structure of $ZrV_2D_{4.5}$ resulting in a formation of 28-vertexes polyhedron ZrD_{28} which is formed as a superposition of two discussed earlier polyhedra RD_4 and RD_{24} (Fig. 1). Because of mutual blocking between the 32*e* (RT_3) and 96*g* (R_2T_2) sites, an increase in the number of vertices from 24 to 28 does not lead to the increase in achievable H storage capacity of the $MgCu_2$-type structure. The spatial stacking of ZrD_{28} polyhedra proceeds via sharing of the hexagonal faces, similar to the situation for the 24-vertex polyhedron.

All so far known order–disorder transitions in the C15-type hydrides are associated with H ordering in the R_2T_2 interstices. This ordering can be described through the formation of occupied and vacant sites in the initial 24-vertex polyhedron having a random occupation of all sites by H (D) (Fig. 3). The known types of ordering result in a formation of 8-vertex (HfV_2D_4 [12] and $ZrCr_2D_{3.8}$ [13]), 12-vertex ($YMn_2D_{4.5}$ [14]) and 18-vertex ($YFe_2D_{3.5}$ [15]) polyhedra (see Fig. 3 and Table 2). The ordering of hydrogen sublattice is complete with the occupancies of D sites approaching or equal to 1 (see Table 1) or partial with limiting values of D occupancies for some sites not exceeding 1/2.

Fig. 3 presents four types of D-polyhedra which are formed from the initial 24-vertex one during hydrogen ordering. Those include two types of polyhedra with a complete hydrogen ordering and all D···D distances exceeding 2 Å: 8-vertex polyhedron $(Hf,Zr)D_8$ in the structures of HfV_2D_4 and $ZrCr_2D_{3.8}$ and 12-vertex polyhedron $Y1D_{12}$ in the structure of $YMn_2D_{4.3}$. Two other existing RD_x polyhedra, YD_{18} ($YFe_2D_{3.5}$) and $Y2D_{12}$ ($YMn_2D_{4.3}$) contain half or even less occupied H (D)-sites and, also, completely ordered vacancies. The ordering of vacancies is clearly seen for $YFe_2D_{3.5}$ (Fig. 3), where one from four hexagons is non-occupied by D-atoms.

Analysis shows that the type of 8-vertex polyhedron is

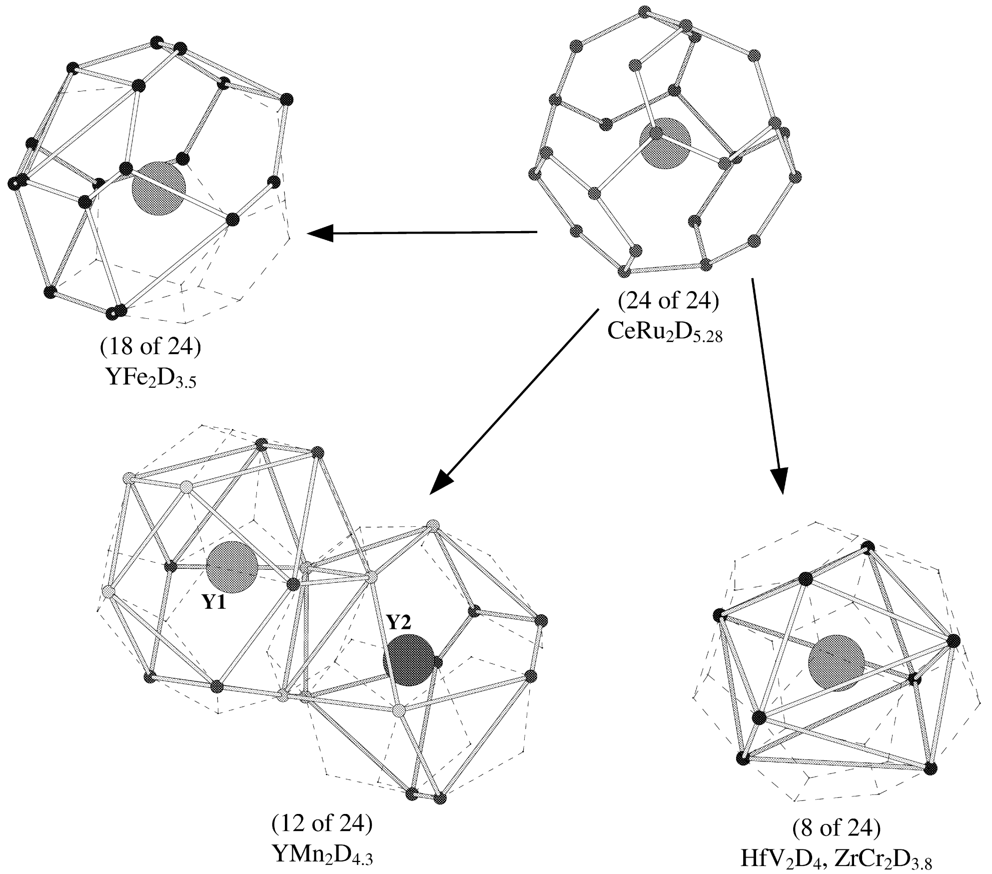

Fig. 3. Interrelations between RD_{24} polyhedron in the cubic disordered $CeRu_2D_{5.28}$ and RD_x polyhedra in ordered (partially ordered) structures of HfV_2D_4, $ZrCr_2D_{3.8}$, $YFe_2D_{3.5}$ and $YMn_2D_{4.3}$.

Table 2
Characteristics of the crystal structures of hydrides with ordered hydrogen sublattice

Deuteride and its symmetry	Relations between the unit cells	x in [RH_x]
Ordered:		
Tetragonal HfV_2D_4	$\vec{a} = 1/2\ (\vec{a}_c{}^{a} - \vec{b}_c)$ $\vec{b} = 1/2\ (\vec{a}_c + \vec{b}_c)$	8
Tetragonal $LaMg_2D_7$	$\vec{c} = 1/2\ (\vec{a}_c - \vec{b}_c) + \vec{c}_c$ $V \approx 1/2\ V_c$	12
Monoclinic $ZrCr_2D_{3.8}$	$\vec{a} = 1/2\ (\vec{a}_c - \vec{b}_c) - \vec{c}_c$ $\vec{b} = 1/2\ (\vec{a}_c + \vec{b}_c)$ $\vec{c} = 1/2\ (\vec{a}_c - \vec{b}_c) + \vec{c}_c$ $V \approx V_c$	8
Partially ordered:		
Rhombohedral $YMn_2D_{4.3}$	$\vec{a} = 1/2\ (\vec{b}_c - \vec{c}_c)$ $\vec{b} = 1/2\ (\vec{a}_c - \vec{c}_c)$ $\vec{c} = 1/2\ (\vec{a}_c + \vec{b}_c)$ $V \approx 1/4\ V_c$	12
Trigonal $YFe_2D_{3.5}$	$\vec{a} = 1/2\ (\vec{a}_c - \vec{c}_c)$ $\vec{b} = 1.2\ (\vec{b}_c - \vec{c}_c)$ $\vec{c} = \vec{a}_c + \vec{b}_c + \vec{c}_c$ $V \approx 3/4\ V_c$	18

[a] a_c, b_c, c_c, V_c, unit cell dimensions and volume for the cubic $MgCu_2$-type cell.

the same for both tetragonal HfV_2D_4 and monoclinic $ZrCr_2D_{3.8}$. In the cubic structure all R···D distances in the 24-vertex polyhedron are equivalent. Tetragonal or monoclinic distortion leads to a different deformation of both metallic and hydrogen sublattices. As a result, two sets of Hf···D distances can be found in the tetragonal structure, while in the monoclinic structure all eight Zr···D bonds inside the ZrD_8 polyhedron become non-equivalent. The stacking of RD_8 polyhedra in these structures proceeds through the sharing of common edges. The RD_8 polyhedra in the monoclinic $ZrCr_2D_{3.8}$ (Fig. 4b) are connected in a more complex way compared to those in the tetragonal HfV_2D_4 (Fig. 4a), thus leading to a unit cell with a two times bigger volume for the former structure (see Table 2).

Hydrogen sublattice in the structure of $YMn_2D_{4.3}$ is formed by altering stacking of the $Y1D_{12}$ and $Y2D_{12}$ coordination polyhedra which share common triangular faces (Fig. 5a). These polyhedra differ from each other by the orientation of the triangular faces. In the $Y1D_{12}$ polyhedron all D···D distances exceed 2 Å limit, whereas in the $Y2D_{12}$ hydrogen atoms form a D···D pair (shown as darker circles in Fig. 3) with a separation of 1.05 Å only, thus limiting the occupancy of this site to 1/2 due to the blocking effect.

Hydrogen sublattice in the structure of $YFe_2D_{3.5}$ contains layers formed from YD_{18} polyhedra, which are connected with each other by sharing occupied hexagons (Fig. 5b). These layers are perpendicular to [001], with the shortest D···D interlayer separation of 2.76 Å.

As has been mentioned before, not more than 12 vertices in the RH_{24} polyhedron formed by 96*g* R_2T_2 sites of the $MgCu_2$-type structure can be filled simultaneously because of the H···H blocking effect. Such 50% occupancy corresponds to the hydrogenation capacity of 6 at. H/f.u. Mutual blocking of the occupied sites occurring during stacking of such RH_{24} polyhedra does not allow to reach experimentally such a capacity. However, a flexibility of H sublattice filling 96*g* sites creates two different ways to

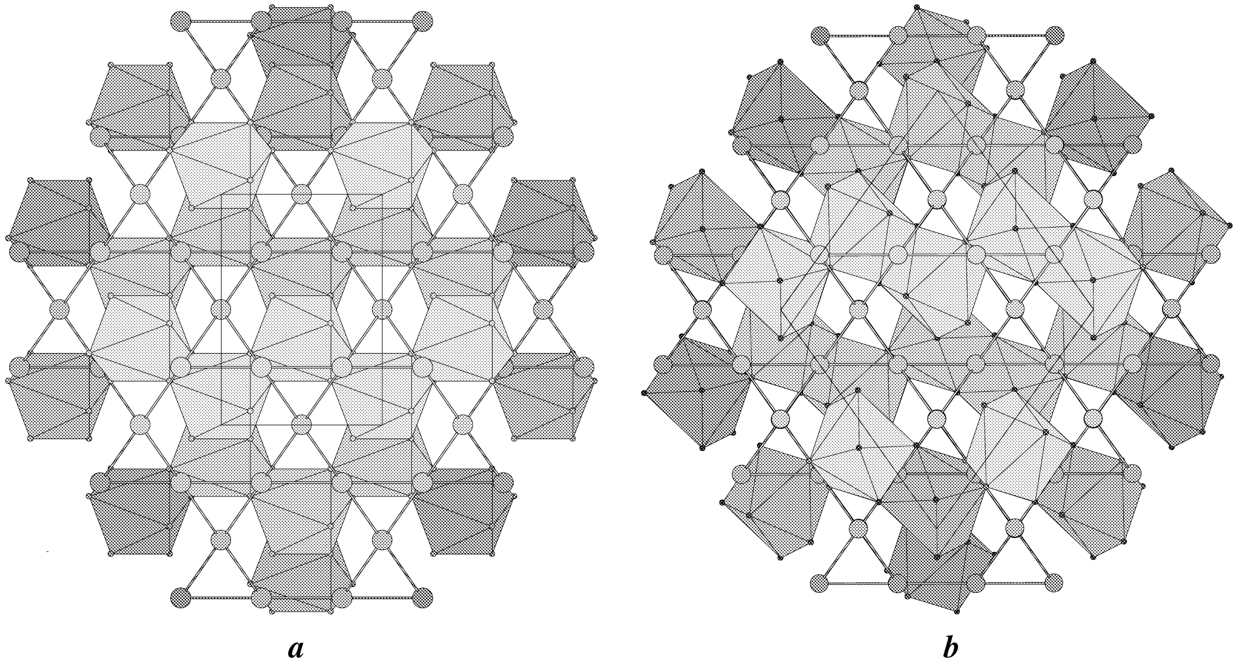

Fig. 4. Stacking of RD_8 polyhedra in the structures of tetragonal HfV_2D_4 (a) and monoclinic $ZrCr_2D_{3.8}$ (b) deuterides, both along [010].

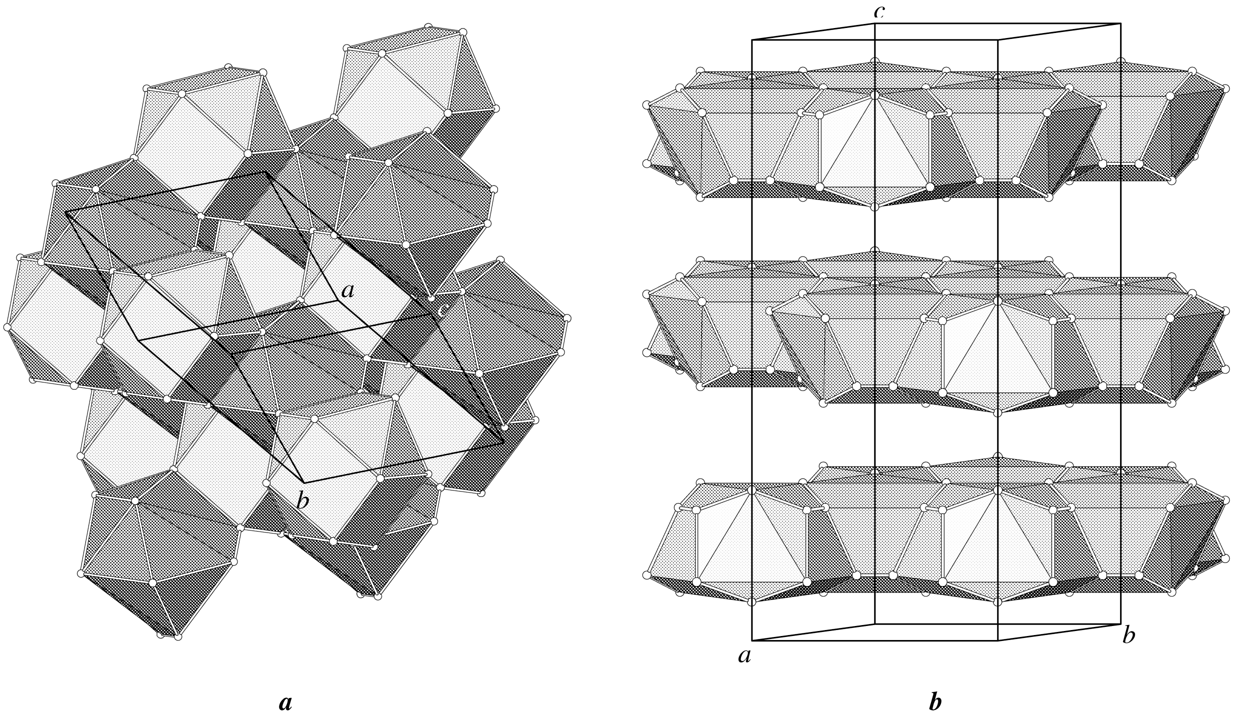

Fig. 5. Two types of YD_{12} polyhedra in the structure of rhombohedral $YMn_2D_{4.3}$ (a) and stacking of YD_{18} polyhedra in the structure of trigonal $YFe_2D_{3.5}$ (b).

form a completely ordered hydrogen distribution with all H···H distances exceeding 2 Å and $H/RT_2 \geq 6$.

These ways are associated with the shifts of hydrogen atom from the centre of 96*g* R_2T_2 site into either R_2T or RT_2 triangular side. Both these triangular sides are common for two neighbouring R_2T_2 sites.

The centre of R_2T triangle is located in the middle of the side of the hexagon (Fig. 6a). Its occupation is observed in the structure of $LaMg_2D_7$ [7]. The LaD_{12} polyhedron formed in the tetragonal $LaMg_2D_7$ is similar to the $Y2D_{12}$ one in the structure of $YMn_2D_{4.3}$. However, a deformation of D sublattice in $LaMg_2D_7$ allows all H···H (D···D) distances to exceed 2 Å, with a subsequent increase in H/RT_2 capacity.

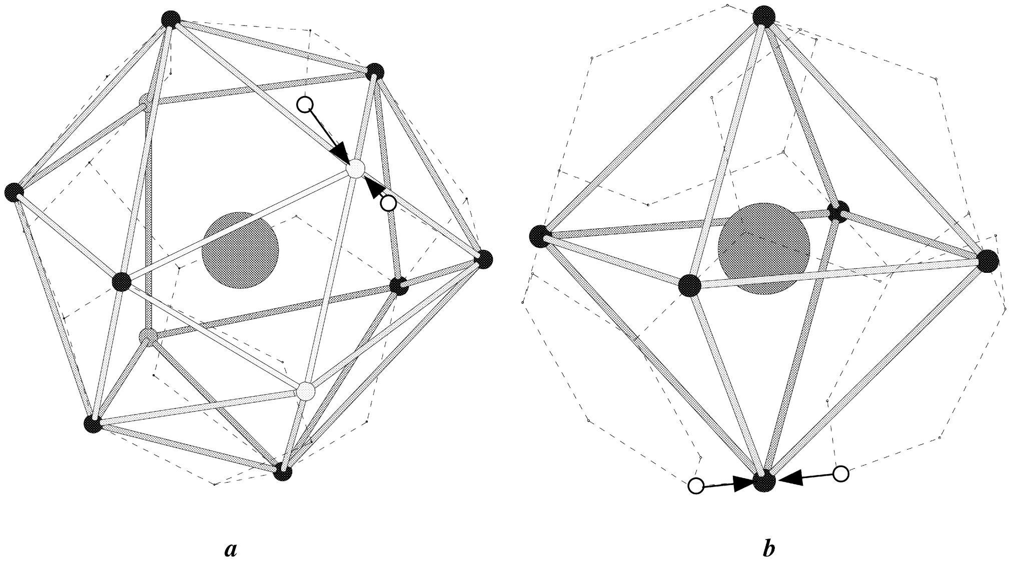

Fig. 6. Modifications of 24-vertex polyhedra due to the displacement of hydrogen atoms from the ideal positions in the centres of R_2T_2 96*g* tetrahedra: shift into the R_2T triangles in the structure of tetragonal $LaMg_2D_7$ (a) and shift into the RT_2 triangles in a possible cubic RT_2H_6 structure (b). In both cases shifts from the ideal 96*g* sites into the triangular sides are shown by arrows.

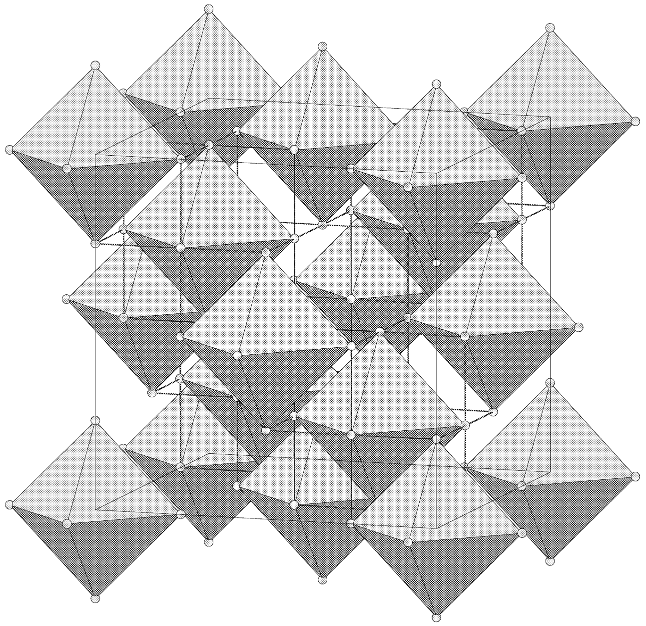

Fig. 7. Possible cubic structure of RT_2H_6 related to the pyrochlore type [16] with H filling the RT_2 faces of R_2T_2 tetrahedra. RH_6 non-connected octahedra with H···H edges of 2.89 Å ($a=7.913$ Å, H in 48*f*: *x* 0 0; $x=0.244$) are shown. Shortest interoctahedral H···H distance is 1.98 Å.

Shift of H atoms into the RT_2 triangular sides is another possibility, which should be considered for the $MgCu_2$-type structures. The centres of such sides are located in between the neighbouring vertices of two hexagons (Fig. 6b). As a result of such a shift, R atoms become octahedrally coordinated by H. The formed RH_6 octahedra are non-connected to each other. The shortest interoctahedral H···H separation is around 2 Å (Fig. 7). The proposed structure is closely related to the known structure of pyrochlore type ($BaCd_2Cl_6$ [16]).

3. Conclusions

In this paper a new approach to the description of hydrogen sublattice in the structures of intermetallic hydrides has been proposed. H sublattice is considered as built from the polyhedra formed by H atoms (sites) around R atoms. A combination of traditional presentation of the structures of intermetallic hydrides as interstitial compounds of hydrogen with H atoms filling available ‘holes’ in the metal sublattice with a proposed ‘H-sublattice and H-polyhedra’ approach, proved to be successful in a description of interrelations between different similar hydride structures. The latter approach plays a dominant role in understanding mutual relations between the structures of intermetallic hydrides with the same structure type of the metal sublattice and in rationalising the occurring order–disorder transitions in the H-sublattice. A detailed analysis has been done for the hydrides formed by $MgCu_2$-type intermetallics and such an approach can be extended further to other structure types of intermetallic hydrides.

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