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Structural Chemistry of Hydrides of Intermetallic Compounds

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The contemporary state of the structural chemistry of the hydrides of intermetallic compounds is discussed. X-ray and neutron diffraction data on hydride phases are surveyed and critically analysed. Tetrahedral and octahedral coordination are shown to be most typical for hydrogen atoms in the structures of multi-component hydride phases. Rules for the structure of intermetallic hydrides are formulated, permitting us to forecast the structures of compounds not yet studied and to predict the maximum capability of the parent intermetallic compounds to absorb hydrogen. 204 references are given.

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I. INTRODUCTION

Compounds of hydrogen with metals are of great interest for the solution of practical and theoretical problems in the new field of science, atom–hydrogen energetics. Metal hydrides can be considered as effective chemical storage and sources of hydrogen, but only if the reaction of hydrogen with the metal in question occurs rapidly and with sufficient completeness under comparatively mild conditions, and the hydrogen weight content in the hydride proves to be high enough.

At pressures up to several kilobars molecular hydrogen reacts only with the limited number of metals which have low ionisation energies: the alkali, alkaline-earth, and lanthanide metals. Titanium, vanadium, and zirconium approach these in respect of their reactivity with hydrogen. It is only recently that a number of unstable hydrides of the transition metals Mn, Fe, Co, Mo, and Rh have been obtained under high pressure conditions[1-5].

However the preparation of hydrides by direct reaction of hydrogen with the metal is not always easily realisable in practice. In the majority of cases the kinetics of absorption and desorption of hydrogen are very sensitive to the presence of minor impurities in both the hydrogen and the metal, the "absorption $\rightleftharpoons$ desorption" equilibrium is established slowly even at relatively high temperatures (300–400 °C), and products with a high content of the primary substance are obtained only in isolated cases.

This is why such great interest was aroused by the discovery at the end of the 1960's of a new type of reaction between hydrogen and intermetallic compounds (IMC) and alloys, one of whose components is a metal capable of forming a stable binary hydride. Chance observations made almost simultaneously by various independent research groups opened up a

new chapter in the chemistry of metal–hydrogen compounds. Their work showed that many IMC's containing Ti, lanthanides (Ln), or Mg react readily with hydrogen at 25–100 °C under 0.1 to 100 atm pressure. The kinetics of this reaction are unique and have no analogy in the chemistry of binary hydrides—the absorption of hydrogen by the metallic phase begins almost immediately and close to room temperature the "absorption ⇌ desorption" equilibrium is as a rule established in a few minutes, depending on the nature of the metallic phase and the purity of its surface.

Up to the present there have been about 500 publications devoted to study of the reaction of various IMC's and alloys with hydrogen. A large amount of experimental data, of interest not only to chemistry but also to those areas of physics, technological and applied sciences bordering on chemistry, has been accumulated. However the structural chemistry of the hydrides remains relatively unstudied—as regards both strictly structural research, little of which was carried out until recently, and also work on the nature of the metal–hydrogen chemical bond.

Finally, structural investigations based on the application of diffraction methods cannot give direct information on the valence state of hydrogen in its compounds with metals, but they are necessary for the development of descriptive crystal chemistry of metal hydrides and they can be very useful (as we have remarked repeatedly) for solving certain definite practical problems connected with the prediction of and search for new polymetallic compositions which absorb a large quantity of hydrogen reversibly at given temperatures and pressures.

The purpose of this review is to discuss the structural chemistry of hydrides containing two or more metal components. Questions of the crystal chemistry and structure of binary hydrides are considered only in so far as they are necessary for the analysis of general rules determining the structure of both binary and more complex hydride phases. We were aware also that substantial reviews of work on the structure of binary metal hydrides have previously been published by Mueller et al.[6], Goldschmidt[7], Mackay[8], Libowitz[9], Stalinski[10], Galaktionova[11], and Andrievskii and Umanskii[12].

II. THE STRUCTURE OF BINARY METAL HYDRIDES

The descriptive crystal chemistry of metal hydrides can be based on the idea that they are unusual "interstitial phases" of hydrogen in a metal lattice-matrix. The alternative view, according to which metal hydrides are regarded as ionic compounds M^+H^-, does not in the majority of cases correspond[12] to the actually observed picture of the structure and physical properties of the hydrides of metals of groups III–VIII.

Analysis of structural relationships in binary hydrides shows that insertion of hydrogen into the metal lattice can occur in two ways:

(1) it is accompanied by a fundamental reorganisation of the metal lattice or in other words by a change in the type of packing of the metal atoms, e.g. by a transition from body-centred cubic (b.c.c.) packing in the structure of the metal itself to face-centred cubic (f.c.c.) packing in the metal sublattice of the hydride; or

(2) it does not lead to a substantial change in the metal structure—in this case the packing of the metal atoms in the metal sublattice of the hydride is no different from the packing in the structure of the metal itself or only an insignificant deformation of the unit cell occurs.

The overwhelming majority of metals react with hydrogen in the first way. It is only for such elements as V, Ni, Nb, Pd, Ta, Ce, and Th that the unit cells of the hydride phases have a simple relationship to or match the original unit cells of the metals.

The hydrogen atoms in the binary metal hydride structures have three types of coordination polyhedra: tetrahedra, octahedra, and triangles. The largest size holes, the octahedral holes in the f.c.c. and the hexagonal close packed (h.c.p.) lattices, are the first to be filled by hydrogen atoms in the structures of hydrides of elements with small atomic radii (metals of groups VI–VIII). However, on passing to the lanthanides, which have considerably larger atomic radii, the tetrahedral holes are filled first and only after that the octahedral. It is only in the structures of HoD_3,[13] YD_3,[14] and Th_4D_{15} [15] that the deuterium atoms have a triangle form of coordination polyhedron.

Thus the general rule of crystal chemistry, that the coordination number (c.n.) of an atom M′ falls as the atomic radius ratio $r_M/r_{M'}$† (r_M/r_H in the present case) increases, is obeyed also in the metal hydride structures—the c.n. of the hydrogen atom changes from 6 to 4 or to 3 as the metal radius increases.

If the M–H(D) interatomic distances in the binary hydride structures are taken to be the sum of the atomic radius of the metal M and the effective radius of the hydrogen atom, it is possible to form a qualitative estimate of the latter#.

It is known that in interstitial structures the size of the holes in the lattice matrix, made up of atoms of radius r_M, increases in the sequence: triangular (c.n. =3; $r_{hole} = 0.22\, r_M$) < tetrahedral (c.n. = 4; $r_{hole} = 0.41\, r_M$) < octahedral (c.n. = 6; $r_{hole} = 0.73\, r_M$).[17] This implies that the radius of the hydrogen atoms, which occupy various types of hole, cannot generally speaking be constant but depends markedly on the type of environment. It is also clear that this effect will be more marked the more complex is the structure of the parent matrix, of metal or an IMC.

These rules are followed in the binary metal hydride structures. The hydrogen atoms with the "largest radius" are those in octahedral holes, their size decreasing with decrease in the metal atom dimensions from 0.7–0.8 Å in lanthanum and cerium hydrides to ~0.6 Å in the hydrides of the metals of groups VI–VIII. The hydrogen atoms with a c.n. of 3 in the $ScH_{2.65}$ structure[18] have the smallest radius (~0.3 Å); this is close to the covalent radius of hydrogen, 0.28 Å.[8] Hydrogen atoms occupying tetrahedral holes have radii in between the values for c.n. 3 and c.n. 6 (0.4–0.5 Å).

The H–H interatomic distances in the structures of binary hydrides of metals of groups VI–VIII are fairly large owing to the low density of hydrogen nuclei in them (~2.6 Å). However, on increasing the hydrogen content in the hydride phases the smallest H–H distances are reduced considerably (to ~2.1 Å in the lanthanide trihydrides and even to ~1.9 Å in the $ScH_{2.65}$ structure).

In conclusion we note a characteristic feature of binary hydride structures: notwithstanding that in the f.c.c. and h.c.p. structures the holes occupied by hydrogen atoms are regular polyhedra, these atoms do not always lie exactly in the centres of the holes. In the hexagonal hydride structures MH_3 and also in $CeD_{2.29}$ [19] the hydrogen atoms are displaced from the centres of both the tetrahedral and octahedral holes, and in the HoD_3 structure this displacement from

†M denotes the element whose atoms have the larger radius and M′ the smaller.

#Values for the metal radii were taken from Pearson[16].

the octahedron centre is so marked that the c.n. of the hydrogen atom becomes equal to 3. The structures of $CeD_{2.51}$ [20] and LaD_3 [21] are particularly representative in this respect; in these, in addition to the shift of the hydrogen atoms from the centres of the octahedral holes, a feature typical of the crystal chemistry of metal hydrides is exhibited: statistical occupation by the hydrogen atoms of a fraction of the crystallographic equivalent positions in the hydride phase structure.

III. GENERAL RULES OF THE REACTION OF HYDROGEN WITH INTERMETALLIC COMPOUNDS

Hydride phases, containing two or more metal components, can be obtained either by hydrogenation of alloys or IMC's of the composition $M_nM'_m$ or by high-temperature synthesis from the binary hydride of one metal and a second metal in an atmosphere of hydrogen. In the latter case a hydride phase $M_nM'_mH_x$ is formed, whereas in the former case three types of reaction are possible[22–24] (the first two of these correspond entirely to the schemes described above for the reaction of individual metals with hydrogen).

1. A compound with a new type of structure is formed.
2. The intermetallic compound absorbs a significant quantity of hydrogen without a substantial deformation of the original crystal structure.
3. There is complete decomposition of the initial IMC and formation of a stable binary hydride MH_x and an intermetallic compound enriched in the metal M′ which is inactive towards hydrogen, with the composition $M_{n-y}M'_m$ (or a hydride phase based on this), or of the metal M′ directly—a hydrogenolysis reaction[23].

The hydrogenolysis reaction of intermetallic compounds does not come within the scope of this review. Therefore the crystal chemistry of the phases formed only by the first or second mechanisms is discussed.

Before proceeding to examine the structural relationships between the IMC and the hydride phases based on them an important feature of IMC structure should be noted. In contrast to the structure of pure metals, in which all the interatomic distances within the range of the closest coordination sphere are as a rule identical, a greater diversity is observed in an IMC—there are distances both shorter and longer than the sum of the respective metal radii, and the variations may be considerable. It will further be shown

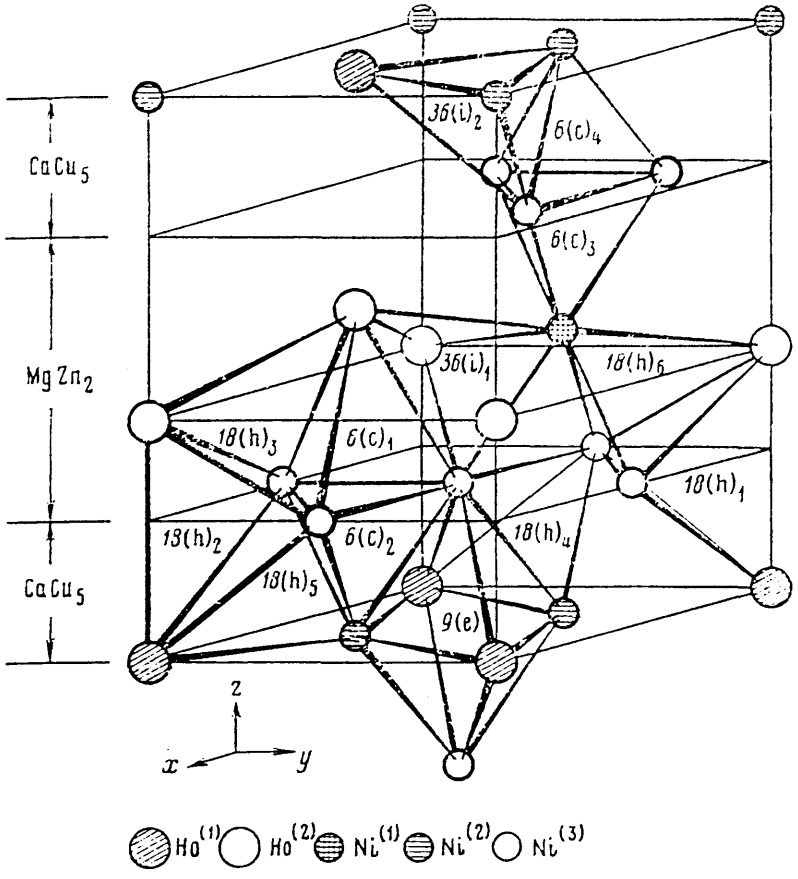


Figure 1. Holes in the $HoNi_3$ structure[40] (the part of the unit cell with $z = 0–1/3$ is shown); the $CaCu_5$ and $MgZn_2$ type sections are marked. The holes (13 different types) are designated by symbols (number of positions and Wyckoff notation) for the equivalent positions in the space group $R\bar{3}m$ corresponding to the centres of the holes.

that the insertion of hydrogen atoms takes place preferentially in those holes whose periphery includes precisely those "long", most easily deformed bonds.

A principal feature of the reaction of IMC's with hydrogen is that, in contrast to metals, in the overwhelming majority of cases the IMC structures do not undergo serious reorganisation on hydrogenation, and the mutual arrangement of the metal atoms in the structure of the hydride phase remains the same, or almost the same, as in the parent IMC.

The structure of hydride phases based on IMC's with structures of the $CaCu_5$, $MgCu_2$ and $MgZn_2$ (Laves phases), $PuNi_3$, Ce_2Ni_7, Gd_2Co_7, Th_6Mn_{23}, Ti_2Ni and CrB types have been investigated most fully. Note that the first six structure types are related and are members of one homologous series of structures MM'_5–MM'_2.[16,25,26] The structures of compounds with a composition intermediate between MM'_5 and MM'_2 can be regarded as consisting of fragments of the $CaCu_5$ and Laves phase type structures. The superposition of these fragments occurs along the [001] direction of the hexagonal unit cell owing to the presence of identical planar nets in the Laves phase and $CaCu_5$ structures. For example, the $PuNi_3$ type structure can be obtained by successively placing one above the other a $CaCu_5$ type unit cell and half of an $MgZn_2$ type unit cell (see Fig.1). As will be shown below, the homologous relationship of these structures predetermines also the similar nature of their reaction with hydrogen.

The hydride phases based on the intermetallic compounds $LaNi_5$ and $CaNi_5$, and also on the alloys $ThNi_3Al_2$, MNi_4Al (M = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho), $MNi_{5-x}M'_x$, where M' = Al, Cr, Fe, Cu,[27–30] retain the hexagonal symmetry of the original MM'_5 structures of the $CaCu_5$ type and the unit cell expands on their formation to an equal extent both in the basal plane and in the [001] direction. Some other structure is evidently possessed by the hydride phases based on the alloys $LaNi_{5-x}Co_x$ (x = 0.5–3.0) because the increase in the unit cell volume occurs mainly through an increase in the lattice parameter a, while the change in the c parameter is insignificant[31].

The hydride phases MCo_5H_x have orthorhombic unit cells which are produced from the original MCo_5 structure by an anisotropic expansion in the basal plane of the hexagonal unit cell with a negligible change in the c parameter[27]. $LaCo_5$ absorbs the largest quantity of hydrogen ($H/LaCo_5$ = 4.3).§ In the γ-hydride so formed the lattice parameter ratio $a/b\sqrt{3} < 1$, in contrast to the hydride phases with $H/MCo_5 < 4$, the so-called β′-, β″-, and β‴-hydrides, for which $a/b\sqrt{3} > 1$.[27] In the β″- and β‴-hydride structures the c parameter is doubled, as indicated in the case of the β‴-hydride by neutron diffraction data. Studies of hydride phases based on alloys of the $La_{1-x}Pr_xCo_5$, $Ce_{1-x}Pr_xCo_5$ and $La_{1-x}Ce_xCo_5$ systems showed[33,34] that they have the β-hydride structure with a doubled c parameter.

The reaction of hydrogen with IMC's of the MM'_2 composition with Laves phase structures, where M is Sc, Y, Ta, Th, a lanthanide, or a Group IV metal and M′ is a transition metal from either period IV or V, has been investigated[30,35–68].

The unit cells retain the original hexagonal symmetry in all cases of hydride phases based on IMC's with the $MgZn_2$ type structure containing Ti, Zr, Er, Lu, and Th as the M component, and also in $ScFe_2$ crystallised with the $MgNi_2$ type structure[30,35–48].

IMC's with $MgCu_2$ type structures react differently with hydrogen. Although in the majority of cases there is an isotropic expansion of the unit cells without a change in their f.c.c. symmetry, for some hydrides of the MM'_2H_x type it was established that there are three different modes of deformation of the original unit cell, leading to unit cells which are primitive cubic with a doubled a parameter[61], orthorhombic with $a \sim b \sim a_{cubic}/\sqrt{2}$ and $c \sim c_{cubic}$,[49,50,54,61] or rhombohedral[66].

With a gradual change in the hydrogen content in the phases ZrV_2H_x and $ZrCr_2H_x$ from $x \sim 0$ up to saturated hydrides the structure of the matrix does not change, but the unit-cell parameters are increased[35]. Analogous results were obtained for YMn_2H_x.[60]

Hydrogenation of MM'_3 compounds (M = lanthanide, Y, Ca) with $PuNi_3$ type structures, when M′ is Co or Ni, leads to formation of di- and tetra-hydride phases and is not accompanied by a change from the symmetry of the original rhombohedral lattices[55,56,68–73]. When hydrogen is absorbed by the intermetallic compound up to the H_2-phase composition there is an expansion of the lattice matrix in the [001] direction of the trigonal unit cell with a negligible change in the a parameter. In the tetrahydride phases, in contrast to the dihydrides, the parameter a increases markedly, i.e. a further increase in the unit cell volume occurs as a result of expansion in the basal plane. When M′ = Fe only one hydride phase, similar to the phase $MCo(Ni)_3H_{\sim 4}$ in composition and crystallographic characteristics, is formed[71,72].

Also, on exceeding a certain critical temperature, below which a two-phase region of α-solid solution and saturated hydride exists, the hydride phases MFe_3H_x (M = Dy, Er)[74–76] acquire the characteristics of a solid solution: a change in their hydrogen content is accompanied by a continuous increase in the unit-cell dimensions.

The data[77] on the existence of the mono- and di-hydrides $DyCo_3H_{1.0}$ and $DyCo_3H_{1.8}$, whose unit cells are "contracted" in the z axis direction as compared to the $DyCo_3$ structure, evidently require experimental verification, since they are not in agreement with other results[70–72].

The $CeCo_3$–H_2 system, in which only one hydride phase $CeCo_3H_3$ is formed, occupies a special place amongst MCo_3–H_2 systems. This phase is analogous in crystallographic characteristics to H_2-phases but the increase in its c parameter is anomalously large, amounting to 32%,[56,72] which is 3–5 times greater than in the dihydrides $MCo(Ni)_3H_{\sim 2}$.

The intermetallic compound $CeNi_3$ which crystallises in an analogous structural type reacts with hydrogen in a similar way—only one hydride phase, $CeNi_3H_3$, is formed and then only the c lattice parameter is substantially increased[56].

Hydrogenation of IMC's of composition M_2Co_7 with the Ce_2Ni_7 and Gd_2Co_7 type structures leads in both cases to formation of two hydride phases $M_2Co_7H_{\sim 3}$ and $M_2Co_7H_{\sim 6}$, but whereas the transition from α-solution to the hydride phase $M_2Co_7H_{\sim 3}$ is accompanied by expansion of the hexagonal (or trigonal) unit cells only in the z axis direction, when the hydride phase $M_2Co_7H_{\sim 6}$ is formed the a parameter increases[56,72].

The hydride phases Ti_2NiH_x (x = 0.5, 1.0, 2.0, 2.5) have been interpreted as individual compounds[78]. However there is no change in the structure of the metal matrix on hydrogenation—the cubic structures of these phases merely have enlarged unit-cell parameters as compared to the original intermetallic compound Ti_2Ni (which crystallises in an analogous structure type). On hydrogenation of the alloys $Ti_2Co_{1-x}Fe_x$,[79] $Ti_2Ni_{1-x}Fe_x$,[80] $Ti_2Ni_{1-x}Co_x$,[80] and the compounds Hf_2M' (M′ = Co, Fe, Mn, Rh),[81,82] which have the same type of structure as Ti_2Ni, the volume of the unit cells of the original structures increases but their cubic symmetry does not change.

The compounds Ti_2Ni, Ti_2Cu, Ti_2Fe, and Ti_2Co are able to absorb oxygen without a change in the initial structure up to the composition $Ti_2M'O_{0.5}$.[83–86] Hydrogenation of the oxygen-containing phases leads to mixed oxyhydride phases whose structures also possess the original cubic symmetry[83–86].

§ With a high pressure of hydrogen (up to 1400 atm) the phase $LaCo_5H_9$ is formed[32].

Judging from neutron-diffraction data[87], several hydride phases are formed on hydrogenation of the intermetallic compound Y_6Mn_{23} with the complex cubic structure of the Th_6Mn_{23} type. The move to phases richer in hydrogen is accompanied by a gradual increase in the volume of the cubic unit cells. However, in most of the work the values of the unit-cell parameters are quoted only for the hydride phases richest in hydrogen[56,57,68,88,89].

The hydride phases based on IMC's with structures of the types CrB ($ZrNiH$,[90] $ZrNiH_3$ [91]), ZrAg ($ZrAgH$ [92]), Th_7Fe_3 ($Th_7Fe_3H_{14.2}$ [93]), $CuAl_2$ (Hf_2NiH_3 [82], Th_2AlD_4 [94]), UNi_5 ($YNi_4.MnH_{4.5}$ [95]), $CeCo_4B$ ($CaNi_4BH_{4.5}$ [55]), CsCl [TiFeH(D),[96,97] $TiFeD_{1.9}$ [98]], Zr_4Al_3 ($Zr_4Al_3H_{4.3}$ [99]), $MoSi_2$ ($Hf_2CuH_{2.8}$, $Ti_2PdH_{2.0}$, $Zr_2PdH_{2.7}$, $Hf_2PdH_{1.9}$ [100]), and Cr_3Si ($V_3GaH_{2.0}$ [101]) also have structures whose unit cells either correspond to the unit cells of the parent IMC structures or are derived from them. In contrast to these, the hydride phases based on the intermetallic compounds TiNi,[78] Mg_2Ni,[102,103] Zr_2Cu,[100] HfCo,[82] HfNi,[82], ZrCo,[104] Ti_3Al,[105] and TiCo [106] have crystal structures whose unit cells are not simply related to those of the parent IMC structures.

The structure of hydride phases obtained by high-temperature synthesis at low hydrogen pressures (~1 atm) from a mixture of the binary hydride of a metal M and a metal M′ have been studied[107–116]. The phases formed are $M_2M'H_{4-6}$ (M = Ca, Sr, Eu, Yb; M′ = Ru, Rh, Ir),[107,108,112,114,115] Sr_2PdH,[110] Sr_2PdH_4 and $Ca_3Pd_2H_4$ [111] with cubic structures and also Li_4RhH_4 and Li_4RhH_5,[116] whose structures possess tetragonal and orthorhombic symmetry respectively; from a mixture of two binary hydrides the phases $LiEuH_3$,[109] $LiBaH_3$ and $LiSrH_3$ [110] with antiperovskite type structures are formed. Saturation of the alloys $ThZr_2$ and $ThTi_2$ with hydrogen at elevated temperatures leads to formation of the phases $ThZr_2H_7$ and $ThTi_2H_6$ and it is accompanied by ordering of the metal atom arrangement as in the Laves phases $MgZn_2$ and $MgCu_2$.[113]

The formation of hydride phases richest in hydrogen leads to a 20–25% increase in the unit-cell volume of the IMC structures, although for a number of structures the ratio $\Delta V/V_0$ exceeds this amount by almost a factor of two (approximately 37% for hydrides based on $CeRu_2$ [143] and $ThMn_2$ [42]). The ratio of the change in the IMC unit-cell volume on hydrogenation ΔV to the number of absorbed hydrogen atoms is close to 2.5–3.5 Å^3 for all the hydride phases studied.

Li_4RhH_4 and Li_4RhH_5 are representative of a few metal hydrides for which an X-ray structure examination has been carried out on single-crystal specimens[116]. In Li_4RhH_4 the c.n. of the hydrogen atom is 6 and its coordination sphere comprises one Rh and five Li atoms forming a distorted octahedron. The structure needs refining by neutron diffraction. The structure of Li_4RhH_5 was not determined so reliably, the positions of all the atoms being deduced from geometrical considerations and from the relationship between the Li_4RhH_4 and Li_4RhH_5 structures.

As a rule, X-ray powder diffraction investigations of the structure of hydride phases do not make it possible to determine the positions in the crystal lattice occupied by hydrogen atoms. To solve this problem it is necessary to use neutron diffraction.

IV. CRYSTAL-CHEMICAL ANALYSIS OF THE STRUCTURES OF INTERMETALLIC COMPOUNDS AS MATRICES FOR THE ADSORPTION OF HYDROGEN

As hydride phases based on IMC's are as a rule powders in which the individual grains are not large enough for them to be used for single-crystal structure determination, neutron powder diffraction has up to the present been used in all the work carried out. The absence of single-crystal specimens creates certain difficulties for the solution of the structure—the traditional methods of structure analysis can be used only in isolated favourable cases to obtain results from a powder diffraction experiment owing to the limited number and overlapping of the reflections in the diffraction pattern. The method of line profile analysis[117] has considerably widened the possibilities of neutron powder diffraction analysis; however its use does not of course enable us to overcome the principal deficiencies of the powder experiment mentioned. The only possible method for solving the structure from the neutron powder diffraction data is to show that there is agreement between the intensities of the reflections calculated theoretically for the proposed model of the structure and those measured experimentally. Since the positions of the metal atoms in the hydride phase structures are close to their positions in the original IMC, the problem becomes one of determining the positions occupied by the hydrogen atoms on entry into the metal lattice.

The principles for constructing the most probable models for the structure of hydride phases based on IMC's can be formulated in the following way[30,40,118].

1. The positions in the parent metal lattice most preferable for filling with hydrogen atoms are the tetrahedral holes with a radius $\geqslant$0.4 Å.

2. The M–H interatomic distances in the IMC hydride lattice are similar to those in the binary hydride lattices; the minimum permissible value is equal to the sum r_M + (0.2 to 0.3) Å.

3. The H–H interatomic distances must not be substantially less than 1.8–2.0 Å.

In addition the following hypotheses are very important when analysing a model for the structure:

4. The preferable holes for occupation are those surrounded to a maximum extent by atoms of the metal M which is more active towards hydrogen (capable of forming a stable binary hydride).

5. The greater the M–M distances between the atoms making up the hypothetical coordination polyhedron in comparison to the sum of the corresponding metal radii, the more easily is this polyhedron deformed and hence the more easily is a hydrogen atom inserted in the hole.

The last hypothesis was put forward *a priori* in 1979 [119] and has been confirmed by an analysis of experimental results obtained over the last three years.

An analysis of possible models for the structures of hydride phases based on IMC's has been carried out, using the hypotheses set out above, for the structure types $CaCu_5$ (on the example $LaNi_5$),[118] $MgCu_2$ (example $ZrCr_2$),[120,121] $MgZn_2$ (example ZrMoFe),[40,121] $PuNi_3$ (example $HoNi_3$),[70] Th_6Mn_{23} (example Y_6Mn_{23}),[87] CrB (examples ZrNi and LaNi),[122–124] and for some other types. Considering that at the present time the structure of the majority of the corresponding hydrides (or deuterides) is already established by neutron diffraction, a detailed account of the results obtained is hardly necessary and so we restrict ourselves to an enumeration of the most characteristic features of the models for the structures of the hydrides of intermetallic compounds which distinguish them from the structures of binary metal hydrides. The main difference is that, as already noted, the number of different types of hole in IMC structures as a rule significantly exceeds the corresponding number in binary hydride structures. Thus, in the $CaCu_5$ type structure there are 5 types of hole suitable in principle for filling by hydrogen atoms[118], in the $MgZn_2$ structure 7 types[40,121], in the Th_6Mn_{23} structure 9 types[87], in the CrB structure 7 types[124], and in the $PuNi_3$ structure (Fig.1) as many as 13 types[70]. The

second, and no less important, difference is that in IMC structures three groups of hole can be distinguished according to the metal atoms surrounding them: (a) holes formed only by atoms of the metal M; (b) holes formed only by atoms of the metal M'; (c) holes with mixed surroundings (metals M and M'), whereas in the binary hydride structures the holes cannot of course be divided into different groups on this basis.

The analysis has shown that insertion of hydrogen atoms in the tetrahedral holes¶ [hM'$_4$] of the parent IMC structures is least probable because, firstly, they are smallest in size and, secondly, they are formed by atoms of the metals M' which are inactive towards hydrogen (nickel, chromium, manganese, molybdenum, or iron). In addition, the M'–M' interatomic distances on the periphery of these holes are as a rule less than double the radius of metal M', so making filling of the holes difficult.

Table 1. Characteristics of the types of hole most preferred for introduction of hydrogen atoms into the structures of $LaNi_5$,[118] $ZrCr_2$,[120] ZrMoFe,[30] $HoNi_3$,[30] Y_6Mn_{23},[87] and LaNi [163] (r is the effective radius of the hole).

Structure	Type of hole	Interatomic distances, Å*			Coordinates**			r, Å	n***
		M – M	M – M'	M'–M'	10^3x	10^3y	10^3z		
$LaNi_5$	[hLa$_2$Ni$_2$]	3.98	4 at 3.20	2.51	107	214	500	0.51	1/2
$ZrCr_2$	[hZr$_2$Cr$_2$]	3.12	4 at 2.99	2.55	815	815	131	0.38	1/2
ZrMoFe	[hZr$_2$(Mo, Fe)$_2$]	3.17	4 at 3.03	2.59	463	926	250	0.39	1
	[hZr$_2$(Mo, Fe)$_2$]	3.17	4 at 3.03	2.59	240	480	250	0.39	1
	[hZr$_2$(Mo, Fe)$_2$]	3.17	2 at 3.03; 2 at 3.04	2.59	544	88	130	0.39	1
	[hZr$_2$(Mo, Fe)$_2$]	3.17	3 at 3.03; 3.04	2.59	283	327	934	0.39	1/2
$HoNi_3$	[hHo$_2$Ni$_2$]	3.42	2 at 2.85; 2 at 3.19	2.48	125	249	73	0.42	1
	[hHo$_2$Ni$_2$]	3.42	2 at 2.85; 2 at 3.19	2.48	875	750	73	0.42	1
Y_6Mn_{23}	[hY$_6$]	6 at 2.54	—	—	0	0	0	0.74	1
LaNi	[hLa$_3$Ni$_2$]	2 at 3.69; 4.36	2 at 2.93; 4 at 2.99	3.81	0	925	250	0.45	1

*According to published data[16], the metal radii (in Å) (for c.n.$_M$ = 12) are as follows: r_{La} = 1.877, r_{Ni} = 1.246, r_{Ho} = 1.766, r_{Zr} = 1.602, r_{Cr} = 1.282, r_{Mo} = 1.400, r_{Fe} = 1.274, r_Y = 1.801.

**Data on the metal atom arrangement in the structures of the parent intermetallic compounds are given in refs. 30, 87, 118, 120, and 163.

***n is the maximum possible occupation factor of the holes under the condition $d_{h\text{-}h} \geqslant 1.8\text{–}2.0$ Å.

¶In this article the method adopted by Soviet authors (see, for example, Kripyakevich's monograph[25]) is used to signify holes (h) and coordination polyhedra of atoms: following specification of a hole or the central atom of the polyhedron (in this article D or H) the metal atoms forming the hole or coordination polyhedron are stated in decreasing order of their radii.

The holes in the parent IMC structures most preferred for filling by hydrogen atoms are the largest: the tetrahedral [hM$_2$M'$_2$] ($LaNi_5$, $ZrCr_2$, ZrMoFe, and $HoNi_3$ structures), the octahedral [hM$_6$] (Y_6Mn_{23} structure) and the hole of form [hM$_3$M'$_2$] at the centre of a trigonal bipyramid (LaNi and ZrNi stuctures), because their periphery involves a high proportion of atoms of the metal M which is active towards hydrogen (Y, Zr, La, Ho) as compared to other holes. In addition, filling of these holes by hydrogen atoms is favoured by the fact that their periphery contains a larger number of M–M distances which exceed the sum of the corresponding metal radii than do other types of hole. The basic data describing the types of hole listed above are given in Table 1.

In the structures under consideration the tetrahedral holes [hMM'$_3$] ($LaNi_5$, $ZrCr_2$, ZrMoFe, $HoNi_3$, and Y_6Mn_{23} structures), [hM$_2$M'$_2$] (Y_6Mn_{23}, LaNi, and ZrNi structures), [hM$_3$M'] (LaNi and ZrNi structures), and the octahedral holes [hM$_2$M'$_4$] ($LaNi_5$ and $HoNi_3$ structures) can also be singled out. If we take into account the dimensions of these holes, the nature of their periphery, and the magnitudes of the distances between the metal atoms forming the holes, we see that they are less likely to be filled than the holes listed in Table 1; however it is quite possible that hydrogen atoms are placed simultaneously in the most preferred holes (see Table 1) and in these latter holes [hMM'$_3$], [hM$_2$M'$_2$], [hM$_3$M'], and [hM$_2$M'$_4$] in hydride phase structures.

The specified hypotheses on the principles for setting up models for the structures of hydride phases have been confirmed by neutron-diffraction studies.

V. NEUTRON-DIFFRACTION STUDIES OF THE CRYSTAL STRUCTURES OF THE HYDRIDE PHASES $M_nM'_mH(D)_x$

The largest number of hydride structure investigations published up to the present are of those based on IMC's with the hexagonal structure of the $CaCu_5$ type[27,40,118,125–134]. Although the introduction of hydrogen into the MM'$_5$ lattice leads to a different deformation of the unit cells in nickel-containing ($LaNi_5D_{6.0}$, $LaNi_4AlD_{4.1}$, etc.) and cobalt-containing ($CeCo_5D_{2.55}$, $PrCo_5D_{3.6}$) hydrides (or deuterides) (see Table 2), all these structures are related to each other and are different versions of the model for the structure of the phase MM'$_5$H(D)$_x$, in which the tetrahedral holes [hM$_2$M'$_2$] and [hMM'$_3$] (or the octahedral holes [hM$_2$M'$_4$]) of the parent IMC lattice are filled. The most substantial differences between the $MNi_{5-y}Al_yD_x$ structures and the MCo_5D_x structures are connected with some displacement of the deuterium atoms from the layers of metal atoms, situated in planes perpendicular to the z axis, since in the MCo_5D_x structures the deuterium atoms are in the planes of these layers (see Figs. 2 and 3). These displacements lead to a change in the form of the coordination polyhedron and the c.n. of the deuterium atoms from 6 in the octahedral [hM$_2$M'$_4$] holes of the MCo_5D_x structures to 4 in the tetrahedral [hMM'$_3$] holes of the $LaNi_5D_{6.0}$ and $LaNi_4AlD_{4.1}$ structures and from 4 in the tetrahedral [hM$_2$M'$_2$] holes of the MCo_5D_x and $LaNi_4AlD_{4.1}$ structures to 3 in the $LaNi_5D_{6.0}$ structure (resulting from displacement of the deuterium atoms into the $LaNi_2$ triangular plane).

For the deuterides MCo_5D_x ordered occupation of two of the six [hM$_2$M'$_2$] holes and two of the three [hM$_2$M'$_4$] holes in the parent lattice is characteristic. Such an occupation evidently explains the anisotropic expansion of the original hexagonal unit cells leading to their orthorhombic deformation. In accordance with structure models proposed for β-hydrides on the basis of neutron-diffraction data[27], β'- and β''-hydrides have the limiting stoichiometric composition MCo_5H_4, but for β'''-hydrides this composition is MCo_5H_3.

Table 2. Details of crystal structures of hydride phases $M_nM'_mH(D)_x$.

Compound	Space group	Lattice parameters, A			C.n. of hydrogen atoms	Coordination polyhedra of hydrogen atoms*	Shortest interatomic distances, A**			Refs.
		a	*b*	*c*			d_1	d_2	d_3	
β′-$PrCo_5D_{3,6}$	*Cmcm*	8.868	5.431	4.083	6 4	O [$D^{(1)}Pr_2Co_4$] T [$D^{(2)}Pr_2Co_2$]	2.38 (0.55)	1.67 (0.42)	2.45	[27]
β″-$NdCo_5D_{2,8}$	*Im2m*	8.819	5.247	8.093	6 4	O [$D^{(1)}Nd_2Co_4$] T [$D^{(2)}Nd_2Co_2$]	2.37 (0.55)	1.43 (0.18)	2.47	[27]
β‴-$CeCo_5D_{2,55}$	*Cmcm*	8.728	5.105	8.146	6 4	O [$D^{(1)}Ce_2Co_4$] T [$D^{(2)}Ce_2Co_2$]	2.34 (0.52)	1.61 (0.36)	2.30	[27]
$LaNi_5D_{6,0}$	*P321*	5.43	—	4.28	4 3	T [$D^{(1)}LaNi_3$] Tr [$D^{(2)}LaNi_2$]	2.44 (0.56)	1.43 (0.18)	2.29	[132]
$LaNi_5D_{6,0}$	*P31m*	5.410	—	4.293	4 4	T [$D^{(1)}LaNi_3$] T [$D^{(2)}La_2Ni_2$]	2.50 (0.62)	1.45 (0.20)	1.57	[125]
$LaNi_5D_{5,6}$	*P31m*	5.40	—	4.28	4 4	T [$D^{(1)}LaNi_3$] T [$D^{(2)}La_2Ni_2$]	2.50 (0.62)	1.56 (0.31)	1.31	[126]
$LaNi_4AlD_{4,1}$	*P321*	5.300	—	4.242	4 4	T [$D^{(1)}LaNi_2$(Ni, Al)] T [$D^{(2)}La_2$(Ni, Al)$_2$]	2.37 (0.49)	1.48 (0.23)	2.09	[133]
$ZrMoFeD_{2,6}$	*P6$_3$/mmc*	5.420	—	8.826	4 4	T [$D^{(1)}Zr_2$(Mo, Fe)$_2$] T [$D^{(2)}Zr_2$(Mo, Fe)$_2$]	1.86 (0.26)	1.78 (0.38)	1.87	[139]
$ZrMn_2D_{3,0}$	*P6$_3$/mmc*	5.391	—	8.748	4 4 4 4	T [$D^{(1)}Zr_2Mn_2$] T [$D^{(2)}Zr_2Mn_2$] T [$D^{(3)}Zr_2Mn_2$] T [$D^{(4)}Zr_2Mn_2$]	2.05 (0.45)	1.74 (0.48)	***	[140]
$ZrCr_2D_{3,5}$	*Fd3m*	7.697	—	—	4	T [DZr_2Cr_2]	2.06 (0.46)	1.73 (0.45)	2.08	[120]
$ZrCr_2D_{3,1}$	*Fd3m*	7.628	—	—	4	T [DZr_2Cr_2]	2.05 (0.45)	1.75 (0.47)	***	[142]
$CeRu_2D_{5,2}$	*Fd3m*	8.383	—	—	4	T [DCe_2Ru_2]	2.40 (0.58)	1.73 (0.39)	***	[143]
$HfV_2D_{4,0}^{****}$	*I4$_1$/a*	5.42	—	7.85	4	T [DHf_2V_2]	2.01 (0.43)	1.82 (0.47)	2,10	[144]
$ZrV_2D_{3,6}^{****}$	*I4$_1$/a*	5.485	—	7.902	4	T [DZr_2V_2]	2.06 (0.46)	1.80 (0.45)	2,10	[145]
$ZrV_2D_{4,5}$	*Fd3m*	7.913	—	—	4 4	T [$D^{(1)}Zr_2V_2$] T [$D^{(2)}ZrV_3$]	2.04 (0.44)	1.81 (0.46)	***	[146]
$ZrV_2H_{3,7}$	*Fd3m*	7.946	—	—	4 4	T [$H^{(1)}Zr_2V_2$] T [$H^{(2)}ZrV_3$]	1.91 (0.31)	1.85 (0.50)	***	[142]
$ZrV_2D_{2,3}$	*Fd3m*	7.910	—	—	4 4	T [$D^{(1)}Zr_2V_2$] T [$D^{(2)}ZrV_3$]	2.04 (0.44)	1.81 (0.46)	***	[142]
$HfV_2D_{4,0}^{*****}$	*Fd3m*	7.78	—	—	4 4	T [$D^{(1)}Hf_2V_2$] T [$D^{(2)}HfV_3$]	1.98 (0.40)	1.79 (0.44)	2.01	[144]
$ZrTi_2D_4$	*Fd3m*	8.19	—	—	4	T [$DZrTi_3$]	1.92 (0.32)	1.92 (0.46)	2.31	[147]
$HoNi_3D_{1,8}$	*R$\bar{3}$m*	4.991	—	26.12	4 4	T [$D^{(1)}Ho_2Ni_2$] T [$D^{(2)}HoNi_3$]	2.14 (0.37)	1.56 (0.31)	2.13	[148]
α-$TiFeD_{0,057}$	*Pm3m*	2.979	—	—	6 (2)	O [DTi_4Fe_2] (L [DFe_2])	2.11 (0.65)	1.49 (0.22)	2.11	[150]
β-TiFeD	*P222$_1$*	2.966	4.522	4.370	6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$]	2.07 (0.61)	1.48 (0.21)	2.29	[97]
$β-TiFeD_{1,1}$	*Pmc2$_1$*	2.956	4.543	4.388	6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$]	1.96 (0.50)	1.49 (0.22)	1.96	[96]
γ-$TiFeD_{1,9}$	*P2/m*	4.704	2.380	4.704 γ=97.0°	6 6 6 6	O [$D^{(1)}Ti_4Fe_2$] O [$D^{(2)}Ti_4Fe_2$] O [$D^{(3)}Ti_4Fe_2$] O [$D^{(4)}Ti_2Fe_4$]	1.99 (0.53)	1.71 (0.44)	2.35	[98]
$TiCuD_{0,9}$	*P4/nmm*	3.020	—	6.837	4	T [DTi_4]	1.93 (0.47)	—	2.14	[157]
Th_2AlD_4	*I4/mcm*	7.629	—	6.517	4	T [DTh_4]	2.39 (0.59)	—	1.79	[94]
$LiPtD_{0,66}$	*P31m*	2.728	—	4.226	4 4	T [$D^{(1)}Li_3Pt$] T [$D^{(2)}LiPt_3$]	1.67 (0.11)	1.56 (0.17)	2.73	[160, 161]
$LiPdD_{0,7}$	*P4/mmm*	2.798	—	3.768	6	O [DLi_2Pd_4]	1.88 (0.32)	1.98 (0.60)	2.80	[160]
$Y_6Mn_{23}D_{23}$	*Fm3m*	12.84	—	—	6 4 4 3	O [$D^{(1)}Y_6$] T [$D^{(2)}Y_3Mn$] T [$D^{3}YMn_3$] Tr [$D^{(4)}Y_2Mn$]	2.02 (0.22)	1.68 (0.42)	***	[87]

Table 2 (cont'd).

Compound	Space group	Lattice parameters, A			C.n. of hydrogen atoms	Coordination polyhedra of hydrogen atoms*	Shortest interatomic distances, A**			Refs.
		a	*b*	*c*			d_1	d_2	d_3	
$Th_6Mn_{23}D_{16.2}$	*Fm3m*	12.92	—	—	6 4 5	O [$D^{(1)}Th_6$] T [$D^{(2)}Th_3Mn$] TB [$D^{(3)}Th_2Mn_3$]	2.34 (0.54)	1.68 (0.42)	***	[158]
$ZrNiH_3$	*Cmcm*	3.53	10.48	4.30	3 4	Tr [$H^{(1)}ZrNi_2$] T [$H^{(2)}Zr_3Ni$]	1.93 (0.33)	1.77 (0.52)	2.04	[91]
$ZrCoD_3$	*Cmcm*	3.53	10.48	4.30	5 4	TB [$D^{(1)}Zr_3Co_2$] T [$D^{(2)}Zr_3Co$]	2.13 (0.53)	1.68 (0.43)	2.20	[104]
$LaNiD_{3.7}$	*Cmcm*	3.98	11.94	4.87	5 4 2	TB [$D^{(1)}La_3Ni_2$] T [$D^{(2)}La_3Ni$] L [$D^{(3)}Ni_2$]	2.41 (0.53)	1.56 (0.31)	2.28	[163]
Sr_2RuD_6	*Fm3m*	7.60	—	—	5	TP [DSr_4Ru]	2.69 (0.54)	1.77 (0.43)	2.50	[114]
Mg_2NiD_4*****	*Fm3m*	6.49	—	—	5	TP [DMg_4Ni]	2.30 (0.70)	1.47 (0.22)	2.07	[164]
$ZrVFeD_{3.6}$	$P6_3/mmc$	5.431	—	8.863	4 4 4 4	T [$D^{(1)}Zr_2(V, Fe)_2$] T [$D^{(2)}Zr_2(V, Fe)_2$] T [$D^{(3)}Zr_2(V, Fe)_2$] T [$D^{(4)}Zr(V, Fe)_3$]	2.02 (0.42)	1.70 (0.35)	***	[166]
$ZrVCuD_{4.0}$	$P6_3/mmc$	5.468	—	8.940	4 4 4 4	T [$D^{(1)}Zr_2(V, Cu)_2$] T [$D^{(2)}Zr_2(V, Cu)_2$] T [$D^{(3)}Zr(V, Cu)_3$] T [$D^{(4)}(V, Cu)_4$]	1.81 (0.21)	1.64 (0.20)	***	[166]
$ZrVNbD_{5.4}$	$P6_3/mmc$	5.690	—	9.288	4 4 4 4	T [$D^{(1)}Zr_2(V, Nb)_2$] T [$D^{(2)}Zr_2(V, Nb)_2$] T [$D^{(3)}Zr_2V(V, Nb)$] T [$D^{(4)}ZrV(V, Nb)_2$]	1.93 (0.33)	1.74 (0.27)	***	[166]
$LaNi_{4.5}Al_{0.5}D_{4.5}$	$P6/mmm$	5.431	—	4.236	4 5	T [$D^{(1)}La_2(Ni, Al)_2$] TB [$D^{(2)}La_2Ni_2(Ni, Al)$]	2.49 (0.61)	1.61 (0.18)	***	[170]
$Ti_4Fe_2OD_{2.25}$	*Fm3m*	11.41	—	—	6 4 4	O [$D^{(1)}Ti_6$] T [$D^{(2)}Ti_3Fe$] T [$D^{(3)}Ti_3Fe$]	1.80 (0.34)	1.51 (0.24)	***	[171]
Sr_2IrD_5	*I4/mmm*	5.320	—	7.796	5 5 5	TP [$D^{(1)}Sr_4Ir$] TP [$D^{(2)}Sr_4Ir$] TP [$D^{(3)}Sr_4Ir$]	2.71 (0.56)	1.69 (0.35)	2.39	[174]

*Symbols for polyhedra: O octahedron, T tetrahedron, Tr triangle, TB trigonal bipyramid, TP tetragonal pyramid, L linear.

**$d_1 = d_{M-H}$, $d_2 = d_{M'-H}$, $d_3 = d_{H-H}$. The values in parentheses after d_1 and d_2 are the effective radius of hydrogen, calculated from $r_{H(D)} = d_{M(M')-H(D)} - r_{M(M')}$.

***The shortest H–H distances cannot be determined precisely from the published data because in the structures there are statistically occupied hydrogen atom positions 1.0–2.1 Å apart.

****Low-temperature modification.

*****High-temperature modification.

However, from data on the absorption–desorption isotherm of hydrogen from the same paper[27], with a rise in pressure the composition of the β′- and β‴-hydrides approaches MCo_5H_4 and MCo_5H_3 respectively, but for β‴-hydrides it does not exceed MCo_5H_3, which contradicts the proposed model for the structure [This sentences does not make sense. The Russian probably has a misprint, possibly in the primes (Ed.of Translation)].

In the structures of the β″- and β‴-hydrides the octahedral holes are filled to a lesser degree as compared to the β′-hydride, while for the β‴-deuteride $CeCo_5D_{2.55}$ ordered filling of half of the [hCe_2Co_4] holes occupied in the β′-hydride structure is characteristic[27]. This ordering, and also some deformation of the metal sublattice in the structures of the β″- and β‴-hydrides, leads to doubling of the *c* parameter of their unit cells.

The orthorhombic γ-hydride structure $LaCo_5H_{4.3}$ has not yet been elucidated although a neutron diffraction study has been carried out on it[27].

A number of publications have been devoted to an investigation of the structure of $LaNi_5D_{6+x}$.[40,118,125–128,132,134]. This is partly because the structure of $LaNi_5H(D)_6$ has been studied independently and also simultaneously in the USSR,[118]

Switzerland[125], and Norway[126].† In addition some inaccuracies in the earlier work gave rise to the need for new publications[129,132]. All the structural models proposed for $LaNi_5.D_{6+x}$ differ rather substantially from each other in some of their features, although each of them is quite satisfactorily verified by the specific neutron-diffraction results of the different authors.

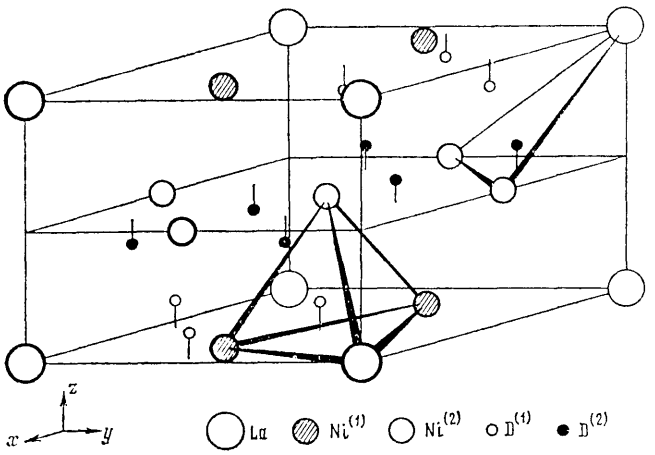


Figure 2. Structure of $LaNi_5D_{6.0}$;[132] the coordination polyhedra of the D atoms are outlined.

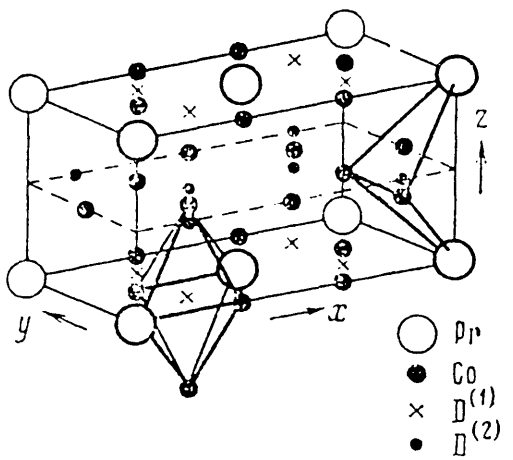


Figure 3. Structure of β'-$PrCo_5D_{3.6}$;[27] the coordination polyhedra of the D atoms are outlined.

†Although the earliest publication on the structure of $LaNiD_{6.8}$ was that of Bowman and co-workers in 1973,[134] their results cannot be considered reliable because of the presence in their structure of D–D and Ni–D interatomic distances equal to 1.30 and 1.17 Å: such small distances are inadmissible from stereochemical considerations; the latter distance is less than the metallic radius of nickel (1.246 Å [16]).

In this situation only those structural results which correlate satisfactorily with the results of research on hydride phases by physicochemical analysis methods can be considered sufficiently conclusive. The broad line n.m.r. method is very informative for crystalline hydrides. The magnitudes of the second moments M_2 determined by this method depend on the H–H and La–H interatomic distances in the hydride phase and indicate clearly the presence of short interatomic contacts. M_2 has been measured experimentally and the values, 12.7 G^2 for $LaNi_5H_{6.0}$ [136] and 13.4 G^2 for $LaNi_{5.3}H_{6.0}$,[135] do not agree with the value M_2 = 20.1 G^2 calculated theoretically by us for the model of the $LaNi_5H(D)_6$ structure proposed by Fischer et al.[125] Hence their hypothesis[125] that positions 6(*d*) in space group *P*31*m* are statistically occupied by deuterium atoms, leading to H–H interatomic distances of 1.58 and 1.68 Å, does not correspond to the facts and the incorrectness of their structural model is indicated.

The same conclusion can be drawn regarding the model proposed[126] for the $LaNi_5D_{5.6}$ structure.

However the model for the $LaNi_5D_{6+x}$ structure proposed[40,132] within the space group *P*321 agrees quite satisfactorily with the experimental n.m.r. results. In considering possible versions of the $LaNi_5H(D)_{6.0}$ structure the assumption was made that in each unit cell the occupation of holes in the metal sublattice by hydrogen atoms proceeds in an ordered way—up to three hydrogen atoms are found in the $[hMM'_3]$ and $[hM_2M'_2]$ holes which are most remote from each other. In this case the minimum H–H interatomic distance is 2.29 Å, which agrees well with the value calculated on the basis of n.m.r. spectra. At the composition $LaNi_5H_{6.0}$ the value calculated for M_2 on this assumption (10.9 G^2) is very close to the experimental values. The n.m.r. results therefore fully confirm the proposed model[40,132] for the $LaNi_5D_{6.0}$ structure.

An argument in favour of this same model is that it is the only model that allows us to explain the presence of the wide homogeneity range in $LaNi_5H_{6+x}$ right up to $LaNi_5H_8$ which exists at −40 °C and a hydrogen pressure of 50 atm,[137] or at room temperature and 1400 atm pressure[32]. In fact the maximum stoichiometric composition which can be achieved by filling all the $[hMM'_3]$ and $[hM_2M'_2]$ holes is $LaNi_5H_9$ whereas in all the other models the composition $LaNi_5H_{6.0}$ cannot be exceeded because of the occurrence of H–H contacts of ~1.5 Å.

The recently published results on the structures of $LaNi_5.D_{6.0}$ and $LaNi_{5-y}M'_yD_x$ (M' = Al, Mn) [127,129] cannot apparently be considered reliable. The authors draw the conclusion that all forms of hole present in the MM'_5 structure including those such as $[hM'_4]$ are statistically occupied by deuterium atoms. However the insertion of hydrogen atoms into holes formed by atoms of elements, which are inactive towards hydrogen and whose binary hydrides are unstable and can be obtained only by the use of special methods, is very improbable. In every case such a conclusion requires careful verification and reliable confirmation by other physicochemical methods as well as structural.

Structural research on hydride phases based on other members of the homologous series of structures MM'_5–MM'_2 has been conducted to a considerably lesser extent than in the case of $MM'_5H(D)_x$. The structure of the hydrides of the Laves phases $MM'_2H(D)_x$ has been studied more completely than the others. The structure of a hydride phase based on an IMC crystallising in the $MgZn_2$ type ($ZrMoFeD_{2.6}$) was first investigated by Yartys' et al.[138,139]. In accordance with the most likely models discussed above for the structure of $MM'_2H(D)_x$ phases, in this deuteride there is ordered insertion of deuterium atoms into two of the four types of $[hZr_2(Mo, Fe)_2]$ holes.

The structure of $ZrMn_2D_{3.0}$ has been investigated (as with ZrMoFe the parent IMC has the $MgZn_2$ type structure).[140] The main results agree with those of Yartys' et al.[138,139]: in $ZrMn_2D_{3.0}$ all four types of $[hZr_2Mn_2]$ hole are statistically occupied.

An attempt to examine the structure of the hydride phase based on $ZrCr_2$, one of whose polymorphic modifications crystallises in the $MgZn_2$ type, was undertaken by Irodova et al.[141] However the authors did not succeed in obtaining a single-phase specimen of the parent IMC and so the structure of the hydride phase was not worked out.

A richer spectrum of structures is obtained by hydrogenating IMC's which crystallise in the $MgCu_2$ type. As in the structures of other Laves phases, there are three different types of hole: $[hM_2M'_2]$, $[hMM'_3]$ and $[hM'_4]$ in the parent $MgCu_2$ structure. For the structures $ZrCr_2D_{3.5}$,[120] $ZrCr_2D_x$ (x = 2.9, 3.1, 3.8),[142] $TiCr_2D_{0.15}$,[49]# $CeRu_2D_{5.2}$,[143] and the low-temperature modifications $HfV_2D_{4.0}$ [144] and $ZrV_2D_{3.6}$,[145] filling of only the largest-in-volume $[hM_2M'_2]$ holes, when their periphery includes the greatest number of atoms of element M (Zr, Ti, Ce, Hf), is characteristic as in hydrides based on IMC's with the $MgZn_2$ type structure. Besides these, two other structural variations are known—a mixed filling of the $[hM_2M'_2]$ and $[hMM'_3]$ holes in the high-temperature modifications of the hydride phases based on HfV_2 and ZrV_2 (the $ZrV_2D_{4.5}$,[146] $ZrV_2H_{3.7}$,[142] $ZrV_2D_{2.3}$,[142] and $HfV_2.D_{4.0}$ [144] structures) and filling of only the $[hMM'_3]$ holes ($ZrTi_2D_4$ structure[147]), as a result of which a spinel type structure is formed§.

It is of interest that in structures with mixed filling of $[hM_2M'_2]$ and $[hMM'_3]$ holes, the degree of filling is identical for zirconium and hafnium compounds. In contrast to $ZrV_2.H(D)_x$ phases in which hydrogen atoms are found in approximately equal or similar quantities in the two types of hole, in the $HfV_2D_{4.0}$ structure five times as many atoms occur in the $[hM_2M'_2]$ holes as in the $[hMM'_3]$ holes. The phase transition which occurs at 298 K in $HfV_2D_{4.0}$ is accompanied by a reduction in the lattice symmetry from f.c.c. to body-centred tetragonal (b.c.t.) and by a redistribution of deuterium atoms in the holes in the metal matrix; the $[hMM'_3]$ holes remain vacant but the $[hM_2M'_2]$ holes are filled in an ordered manner—of the three possible positions which are related by symmetry operations in the f.c.c. unit cell but are independent in the b.c.t. cell, only one is occupied. Similar results were obtained for $ZrV_2D_{3.6}$.[145]

Neutron-diffraction studies of hydride phases based on IMC's located in the homologous series of related compounds between the compositions MM'_5 and MM'_2 have been carried out for only one compound, namely the deuteride $HoNi_3D_{1.8}$ based on an IMC with the $PuNi_3$ type structure[40,148]. As was expected, the structure of $HoNi_3D_{1.8}$ corresponds to one of the most probable models for the structure—a large proportion of the deuterium atoms occupy the $[hHo_2Ni_2]$ holes, which are the most preferred from the point of view of their size and periphery, and which are similar to the holes with the same periphery and which are occupied in the MM'_5D_x deuteride structures, and they are located near the boundary of the $CaCu_5$ and $MgZn_2$ type portions of the structure (Fig.4). However, the most distinctive feature of the $HoNi_3D_{1.8}$ structure is the occupation of holes with an $HoNi_3$ periphery. This type of hole lies within the $MgZn_2$ type section of the structure and is vacant in the $ZrMoFeD_{2.6}$ and $ZrMn_2D_{3.0}$ structures.

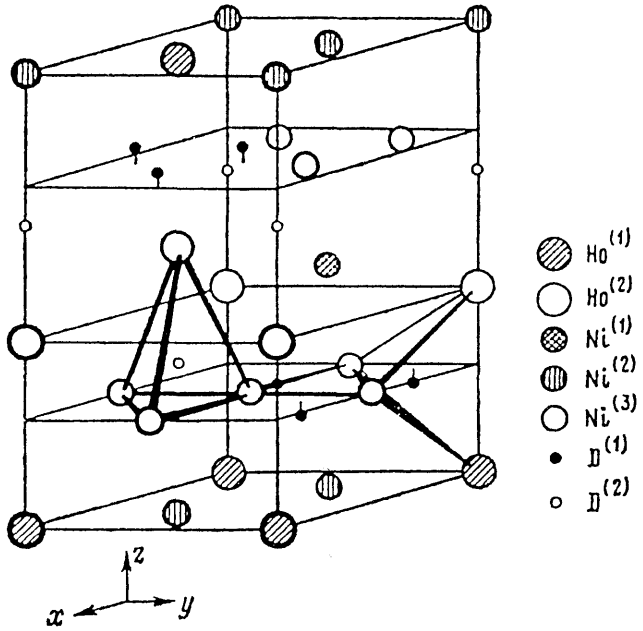


Figure 4. Structure of $HoNi_3D_{1.8}$ [148] (z = 0–1/3); the coordination polyhedra of the D atoms are outlined.

The special features of the structure of $HoNi_3D_{1.8}$ permit the unusual type of deformation of the metal matrix on the insertion of hydrogen into it (expansion of the unit cell only in the z axis direction) to be explained. Analysis of the M–M interatomic distances in the $HoNi_3$ structure shows that they vary over a fairly considerable range—some of them exceed the sum of the corresponding metal radii while other distances are markedly "shortened", i.e. significantly less than the sum of the radii, with all the "shortened" distances lying either in planes perpendicular to the z axis of the unit cell, or at a very small angle to these planes, and the "elongated" distances, on the other hand, lying either parallel to the z axis or at some angle to this axis. It thus seems quite natural to suppose that expansion of the unit cell must take place most easily in that direction where resistance to the deformation resulting from the insertion of hydrogen atoms is least. It is evidently just this ease of deformation of the "elongated" M–M bonds, which lie along the z axis, that explains the expansion of the unit cell only in the [001] direction. The holes in the metal matrix preferred for insertion of hydrogen atoms are of course those whose periphery contains "elongated" M–M bonds. As might have been supposed two of just such holes are occupied in the $HoNi_3D_{1.8}$ structure.

#The stoichiometric composition corresponds to the α-solution.

§Although $ZrTi_2D_4$ is formed by the reaction of deuterium with an alloy of composition $ZrTi_2$ which does not possess the $MgCu_2$ type structure, in the structure of this deuteride the metal atoms occupy crystallographic positions characteristic of a C15 type phase and therefore the $ZrTi_2D_4$ structure can be regarded as a derivative of insertion type in the structure of the hypothetical compound "$ZrTi_2$".

The choice of hydride phases based on other structural types of IMC which have been investigated by neutron diffraction has been to a considerable degree accidental. Much interest has been shown for some time past in the study of the structure of hydride phases formed on the basis of TiFe. This is quite understandable as $TiFeH_{1.9}$ is one of the most promising substances for hydrogen storage[149]. There have been neutron-diffraction studies of all the hydride phases formed in the TiFe–$H(D)_2$ system: α, β, and γ with compositions corresponding to the formulae $TiFeD_{0.057}$,[150] $TiFeD_{1.0-1.1}$,[96,97] and $TiFeD_{1.9}$.[98]

These researches showed that deuteriation is not in this case accompanied by reorganisation of the parent metal matrix and leads only to some deformation. In the α-phase $TiFeD_{0.057}$ [150] there is ordered occupation by the deuterium atoms of one of the three octahedral holes with a Ti_4Fe_2 periphery present in the unit cell of TiFe. The difference between the Fe–D interatomic distances and the metallic radius of iron (0.22 Å) is significantly less than the corresponding value for the Ti–D distances (0.65 Å). The coordination of the deuterium atom can be interpreted as linear $[DFe_2]$ and its coordination number is as a result decreased from 6 to 2.

Further introduction of hydrogen into the structure gives the β-phase which has a composition close to $TiFeH(D)_{1.0}$.[96,97] The orthorhombic $TiFeD_{1.1}$ structure was examined for the first time by neutron diffraction by Thompson et al.[96], who showed that the deuterium atom $D^{(1)}$ occupies the octahedral $[hTi_4Fe_2]$ hole. The small amount of deuterium in excess of the composition $TiFeD_{1.0}$ occurs in octahedral holes of a second type, also having a Ti_4Fe_2 periphery, but they are somewhat displaced from the ideal centres. A second examination of this structure[97] confirmed the main results of Thompson et al.[96], but found that the $D^{(2)}$ atoms are exactly in the centres of the $[hTi_4Fe_2]$ holes.

In the *P–C* diagram of the TiFe–H_2 system[151] two two-phase regions α + β and β + γ exist. However, on the basis of unverified data[152] as to the existence of a subsidiary plateau in the composition range $1 < x < 1.4$ on the isotherm for absorption–desorption of hydrogen by the hydride phase $TiFeH_x$ at 274 K (note that these data were not confirmed in a study of deuterated specimens[153]), Schefer et al.[153] concluded that there is a hydride phase close in composition to $Ti_3Fe_3D_4$. Examination of the structure of this phase showed that it is isostructural with $TiFeD_{\sim 1}$ and further introduction of deuterium atoms into it takes place in the holes filled with the $D^{(2)}$ atoms in the $TiFeD_{\sim 1}$ structure.

The γ-phase $TiFeD_{1.9}$ (Fig. 5) has a monoclinic unit cell in which the deuterium atoms occupy four different positions[98]. Three of these are octahedral holes with a Ti_4Fe_2 periphery, two out of the three corresponding to the positions of atoms $D^{(1)}$ in the β-phase structure, but for atom $D^{(4)}$ the coordination polyhedron is the octahedron $[D^{(4)}Ti_2Fe_4]$. Rather unexpectedly the holes occupied by atoms $D^{(2)}$ in the β-phase structure are vacant in the γ-phase.

The TiFe–$H(D)_2$ system was also studied with neutron diffraction by West German authors[154,155]. The results obtained are on the whole in agreement with the data discussed above[96,97].

A detailed discussion of all the neutron-diffraction data on the TiFe–$H(D)_2$ system has been given in a recent review[156].

$TiCuD_{0.9}$, which has been examined by neutron diffraction[157], was obtained by starting with the γ-modification of the IMC which possesses tetragonal symmetry. Unfortunately the reliability of the experimental results is reduced considerably by the presence as an impurity in the IMC of another of its allotropes, the δ-phase, which also has a tetragonal structure and whose reaction with hydrogen was not studied by these authors. In this connection the exclusion of some parts of the neutron-diffraction pattern (in which the diffraction lines of the γ- and δ-hydrides $TiCuD_x$ were superposed) from consideration was not sufficiently justified. Nevertheless these results are quite reasonable and correspond to the most probable model for the deuteride structure: the holes occupied by hydrogen are those most preferred for filling, the tetrahedral holes $[hTi_4]$ which have a periphery of atoms of the element (titanium) more active with respect to hydrogen.

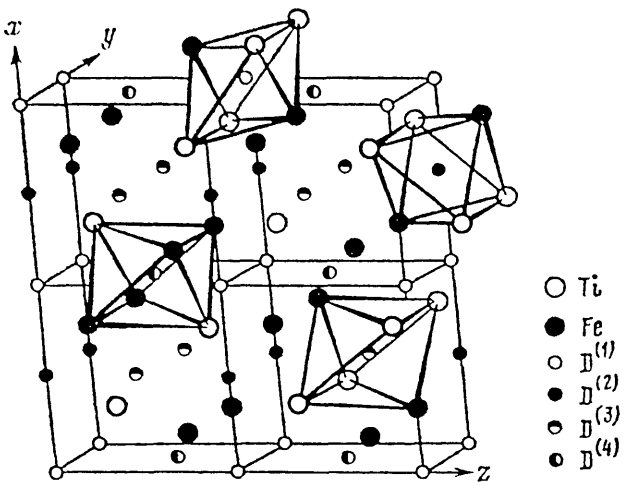


Figure 5. Structure of γ-$TiFeD_{1.9}$; the coordination polyhedra of the D atoms are outlined.

The investigation of the deuterides $Y_6Mn_{23}D_x$ (x = 8.3, 18.0, 23.0) based on an IMC with the Th_6Mn_{23} type structure[87] is of considerable interest. The parent IMC crystallises with a complex cubic structure, the unit cell of which contains 116 metal atoms and has 9 different positions which can be occupied by deuterium atoms. The sequence of filling of the different positions as the deuterium content is increased corresponds on the whole to the rules set out above for the structure of multicomponent IMC hydrides. When the first hydride phase $Y_6Mn_{23}D_{8.3}$ is formed, the deuterium atoms enter the $[hY_6]$ and $[hY_3Mn]$ holes whose periphery contains the largest contribution of atoms of yttrium which is the element active towards hydrogen. In the second phase $Y_6Mn_{23}D_{18}$ the $[hYMn_3]$ holes are filled as well and then in the $Y_6Mn_{23}.D_{22.9}$ structure deuterium atoms enter the $[DY_2Mn]$ position with trigonal planar coordination. As expected, the $[hMn_4]$ holes formed by manganese, which is the inactive element with respect to hydrogen, are not filled in any of the deuterides. From the last of the proposed models we may arrive at the maximum stoichiometric composition for the hydride phase of $M_6M'_{23}H_{33}$.

$Th_6Mn_{23}D_{16.2}$ has been examined by neutron diffraction[158]. The structure of this compound might be expected to be analogous to that of $Y_6Mn_{23}D_{18}$ described above. It was however found that they are not isostructural—firstly, the deuterium atoms are displaced substantially from the centres of the $[hMM'_3]$ holes and two holes of this type are arranged with an Mn_3 triangular face in common, leading to a change in the form of the coordination polyhedron of the deuterium

atom from a tetrahedron in $Y_6Mn_{23}D_{18}$ to a trigonal bipyramid $[D^{(3)}Th_2Mn_3]$. In addition, the degree of occupation of the $[hM_6]$ holes in the structure of the Th compound is relatively small, in contrast to the $Y_6Mn_{23}D_{18}$ structure in which they are completely filled[87].

The intermetallic compound LiPt crystallises in the LiRh type structure[159], which is a superstructure to the Mg type. In the $LiPtD_{0.66}$ structure[160,161] the deuterium atoms occupy the tetrahedral holes in the hexagonal close packing. The coordination polyhedra of the deuterium atoms are the $[D^{(1)}.Li_3Pt]$ and $[D^{(2)}LiPt_3]$ tetrahedra. The $LiPtD_{0.66}$ structure has no analogues among the structures of binary hydrides with hexagonal close-packed metal atoms, for which as is known filling of octahedral, and not tetrahedral, holes is typical.

The intermetallic compound LiPd exists in two polymorphic modifications, with structures of the LiRh and CsCl types[162]. Only one of these (the LiRh type) is capable of reacting with hydrogen, and the hydride formed has a tetragonal structure[160]. The hydrogenation process is accompanied by reorganisation of the metal matrix from the LiRh type to a tetragonally distorted CsCl type. If the $LiPdD_{0.7}$ structure[160] is regarded as derived by insertion to the CsCl type, then the deuterium atoms are found to occupy only one out of three octahedral holes present in the b.c.c. unit cell with Li_2Pd_4 periphery, evidently as a result of which there is an anisotropic expansion of the structure.

The structure of Th_2AlD_4 [94] can be regarded as a packing of $[AlTh_8]$ tetragonal antiprisms with aluminium at the centre and unfilled $[hTh_4]$ tetrahedra, which the hydrogen atoms occupy on introduction into the IMC lattice. At the stoichiometric composition Th_2AlD_4 all 16 of these tetrahedra are occupied but when D/Th_2Al is less than 4 the filling is disordered.

The $ZrNiH_3$ structure[91] is a derivative of the insertion type to the CrB type structure. The structure of ZrNi consists of layers of $[NiZr_6]$ trigonal prisms with nickel at the centre and layers of unoccupied rhombic pyramids and tetrahedra of zirconium atoms alternating one above the other[25]. In the $ZrNiH_3$ structure the hydrogen atoms of one sort are at the centre of the base of the trigonal prisms; their coordination polyhedron is the trigonal bipyramid $[H^{(1)}Zr_3Ni_2]$. The hydrogen atom is displaced from the ideal position at the centre of the bipyramid in the plane passing through the nickel atoms and one of the zirconium atoms. The coordination of the atom $H^{(1)}$ can be regarded as triangular $[H^{(1)}ZrNi_2]$. The hydrogen atoms of the second sort occupy distorted tetrahedra $[H^{(2)}Zr_3Ni]$.

Deuteriation of the intermetallic compound ZrCo, which possesses the CsCl type structure, gives $ZrCoD_3$, isostructural with $ZrNiH_3$, with ordered Zr and Co atoms in the CrB type[104]. In contrast to the $ZrNiH_3$ structure, the atom $D^{(1)}$ is only slightly displaced from the centre of the trigonal bipyramid, so that it has a c.n. of 5, $[D^{(1)}Zr_3Co_2]$. Atom $D^{(2)}$, as in the $ZrNiH_3$ structure, has a c.n. of 4 and tetrahedral coordination $[D^{(2)}Zr_3Co]$.

The third representative of hydride phases based on an IMC with the CrB type structure, whose structure is known, is $LaNiD_{3.7}$. When the D/LaNi ratio exceeds 3.0, the deuterium atoms have linear coordination, which is unusual for metal hydrides, with nickel atoms as neighbours (Fig.6).[124,163] The structure of $LaNiD_{3.7}$, together with $TiFeD_{0.057}$,[150] is a rare example of a metal hydride structure in which the hydrogen atoms have a c.n. of 2. The atoms $D^{(1)}$ and $D^{(2)}$ in this structure occupy the same positions as in the structures of Zr-containing compounds with trigonal bipyramids and tetrahedra as coordination polyhedra.

Sr_2IrD_5 and Sr_2RuD_6 [114] are obtained by deuteriation of a mixture of SrD_2 and Ir (or Ru). Their structures are cubic with the metal atoms ordered in the antifluorite positions. The $Sr_2M'D_{6-x}$ structure (M' = Ir, Ru) can be regarded as a packing of equal numbers of vacant and occupied cubes $[hSr_8]$ and $[M'Sr_8]$. The deuterium atoms are centred over all the cube faces, and their coordination polyhedron is a tetragonal pyramid $[DSr_4M']$. In defect structures ($H/Sr_2M' < 6$) the hydrogen atoms are statistically distributed in the holes. These hydrides are isostructural with K_2PtCl_6.

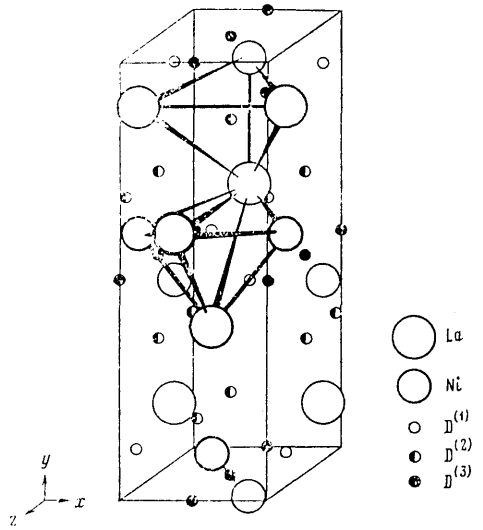


Figure 6. Structure of $LaNiD_{3.7}$; the coordination polyhedra of the D atoms are outlined.

Among compounds crystallising in the K_2PtCl_6 type the greatest defect nature of the hydrogen sublattice is shown by the high-temperature modification of Mg_2NiD_4 [164] (the phase transition is at 483–518 K) which, in contrast to the phases discussed above, can be obtained by starting with Mg_2Ni. In the deuteration process the hexagonal Mg_2Ni structure reorganises to the cubic antifluorite type. However, the defect nature of the sublattice does not lead to a change in the c.n. of the deuterium, which is 5, nor in its coordination ($[DMg_4.Ni]$ tetragonal pyramid).

The details of the crystal structures of the hydride phases described above are given in Table 2, and the crystallographic data for the parent IMC's and hydride phases based on them are in Table 3.

Table 2 shows the shortest M–H and H–H interatomic distances as well as the symmetry of the structures and the form of the coordination polyhedron of the deuterium atoms. In the majority of the structures the mean values of the M–H(D) distances are equal to the sum: r_M + 0.4 to r_M + 0.6 Å. They are as a rule similar in size to the analogous distances in the structures of binary hydrides.

However, for half of the structures in Table 2 (to be precise, 17 out of 35) the minimum effective radius of the hydrogen atom is substantially less, lying in the ranges 0.18 to 0.26 Å (10 structures) or 0.27–0.33 Å (7 structures), and a comparable value occurs for only two binary hydrides (0.31 to 0.32 Å in Y and Sc trihydrates[18,14]).

Table 3. Crystallographic data for hydride phases $M_xM'_yH_z$ and the parent intermetallic compounds.

IMC	Structure type	Lattice parameters, A			$H/M_xM'_y$	Lattice parameters, A			$\Delta L/V_0$, %	ΔV/atoms of H, A^3	Refs.
		a	*b*	*c*		*a*	*b*	*c*			
LiSr	*	—	—	—	3.0	3.833	—	—	—	—	[110]
Li_4Rh	*	—	—	—	4.0	6.338	—	4.413	—	—	[116]
Li_5Rh	*	—	—	—	5.0	3.380	9.020	8.895	—	—	[116]
LiBa	*	—	—	—	3.0	4.023	—	—	—	—	[110]
LiEu	*	—	—	—	3.0	3.796	—	—	—	—	[110]
Mg_2Ni**	Mg_2Ni	5.19	—	13.22	4.0	6.497	6.414	6.601	33.6	4.3	[102]
Mg_2Ni	Mg_2Ni	5.19	—	13.22	4.0	6.490	—	—	33.0	4.2	[102]
$CaNi_2$	$MgCu_2$	7.251	—	—	3.4	7.7	—	—	19.8	2.8	[55]
$CaNi_3$	$PuNi_3$	5.030	—	24.27	4.6	5.444	—	26.56	28.2	3.6	[55]
$CaNi_5$	$CaCu_5$	4.950	—	3.936	4.5	5.305	—	4.009	17.0	3.2	[55]
$CaNi_5$	$CaCu_5$	4.950	—	3.936	5.0	5.250	9.194	8.042	16.2	2.7	[177]
Ca_2Ru	*	—	—	—	6.0	7.24	—	—	—	—	[114]
Ca_2Rh	*	—	—	—	5.0	7.24	—	—	—	—	[114]
Ca_2Pd_2	*	—	—	—	4.0	5.22	—	—	—	—	[111]
Ca_2Ir	*	—	—	—	5.0	7.29	—	—	—	—	[114]
$CaNi_4B$	$CeCo_4B$	5.066	—	6.846	3.5	5.256	—	7.021	10.4	2.3	[55]
$ScMn_2$	$MgZn_2$	5.033	—	8.278	3.8	5.49	—	8.96	28.8	3.4	[45]
$ScFe_{1.96}$	$MgZn_2$	4.965	—	8.125	2.0	5.279	—	8.507	18.4	4.0	[187]
$ScFe_2$	$MgNi_2$	4.972	—	16.28	2.7	5.255	—	17.04	16.9	2.7	[44]
$ScCo_2$	$MgCu_2$	6.922	—	—	2.8	7.334	—	—	18.9	2.8	[44]
$ScNi_2$	$MgCu_2$	6.934	—	—	1.6	7.141	—	—	21.2	2.4	[44]
Ti_3Al	Mg_3Cd	5.793	—	4.655	1.4	3.28	—	—	10.6	1.3	[105]
Ti_3Al	Mg_3Cd	5.793	—	4.655	6.4	4.35	—	—	6.4	0.8	[105]
$TiCr_{1.8}$	$MgCu_2$	6.94	—	—	3.4	7.30	5.18	4.94	11.6	1.5	[49]
$TiCr_{1.9}$	$MgZn_2$	4.927	—	7.961	2.9	5.171	—	8.518	17.4	5.2	[48]
TiFe	CsCl	2.975	—	—	1.0***	2.966	4.522	4.369	11.4	3.0	[97]
TiFe	CsCl	2.975	—	—	1.1***	2.956	4.543	4.388	12.0	3.1	[96]
TiFe****	CsCl	2.975	—	—	1.9***	4.704	2.830	4.704	18.2	2.5	[98]
TiCo	CsCl	2.994	—	—	1.0	6.44	—	9.06	6.2	1.7	[106]
TiNi	CsCl	3.013	—	—	1.0	24.8	—	—	8.7	2.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	0.5	11.50	—	—	4.8	4.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	1.0	11.90	—	—	7.6	3.4	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	2.0	11.80	—	—	13.3	3.0	[78]
Ti_2Ni	Ti_2Ni	11.32	—	—	2.5	11.90	—	—	16.2	2.9	[78]
TiCu	TiCu	3.108	—	5.887	0.9***	3.02	—	6.837	9.0	2.8	[157]
Ti_2Pd	$MoSi_2$	3.090	—	10.054	2.0	2.96	3.16	11.39	10.9	2.6	[100]
V_3Ga	Cr_3Si	4.818	—	—	2.0	4.959	—	—	9.1	2.5	[101]
Sr_2Pd	*	—	—	—	1.0	7.97	—	—	—	—	[110]
Sr_2Pd	*	—	—	—	4.0	9.96	—	—	—	—	[111]
Sr_2Ir	*	—	—	—	5.0	7.62	—	—	—	—	[114]
YMn_2	$MgCu_2$	7.680	—	—	2.9	8.163	—	—	20.1	3.9	[57]
YMn_2	$MgCu_2$	7.680	—	—	2.9	8.274	—	—	25.0	4.9	[57]
YMn_2	$MgCu_2$	7.680	—	—	*****	8.27	—	—	24.9	—	[60]
Y_6Mn_{23}	Th_6Mn_{23}	12.44	—	—	25	12.84	—	—	10.0	1.9	[57]
YFe_2	$MgCu_2$	7.348	—	—	2.0	7.679	—	—	14.1	3.5	[185]
YFe_2	$MgCu_2$	7.348	—	—	3.6	16.07	—	—	30.8	4.2	[185]
YFe_2	$MgCu_2$	7.356	—	—	4.2	7.84	—	—	21.1	2.5	[56]
YFe_3	$PuNi_3$	5.137	—	24.61	4.8	5.375	—	26.46	17.9	2.3	[56]
Y_6Fe_{23}	Th_6Mn_{23}	12.12	—	—	21.5	12.47	—	—	8.3	1.7	[56]
YCo_2	$MgCu_2$	7.214	—	—	3.6	15.54	—	—	12.5	3.2	[61]
YCo_3	$PuNi_3$	5.013	—	24.35	1.0	5.013	—	25.86	6.2	3.7	[56]
YCo_3	$PuNi_3$	5.013	—	24.35	2.0	5.000	—	26.23	7.2	2.1	[70]
YCo_3	$PuNi_3$	5.013	—	24.35	3.7	5.268	—	26.46	20.0	3.2	[70]
Y_2Co_7	Gd_2Co_7	5.002	—	36.15	1.5	4.988	—	37.72	3.8	3.3	[72]
Y_2Co_7	Gd_2Co_7	5.002	—	36.15	3.0	5.138	—	38.45	11.6	5.0	[72]
YNi_2	$MgCu_2$	7.154	—	—	3.0	7.569	—	—	18.4	2.6	[185]
YNi_2	$MgCu_2$	7.184	—	—	3.6	7.563	—	—	17.7	2.3	[56]
YNi_3	$PuNi_3$	4.973	—	24.42	1.2	4.996	—	24.35	0.6	0.3	[56]
YNi_3	$PuNi_3$	4.977	—	24.44	1.6	4.987	—	26.82	13.2	4.6	[188]
YNi_3	$PuNi_3$	4.973	—	24.37	4.0	5.267	—	26.57	22.3	3.2	[73]
YNi_3	$PuNi_3$	4.977	—	24.44	4.2	5.283	—	26.82	25.0	3.4	[190]
YNi_4Mn	UNi$_5$	6.972	—	—	4.5	7.3	—	—	7.4	2.8	[95]
Zr_4Al_3	Zr_4Al_3	5.433	—	5.390	3.6	5.484	—	5.595	5.7	2.2	[99]
ZrV_2	$MgCu_2$	7.446	—	—	4.8	7.956	—	—	23.5	2.5	[39]
$ZrCr_2$	$MgZn_2$	5.106	—	8.273	2.7***	5.367	—	8.754	16.9	2.9	[40]
$ZrCr_2$	$MgCu_2$	7.207	—	—	3.5***	7.697	—	—	21.9	2.9	[120]
$ZrMn_{1.8}$	$MgZn_2$	5.045	—	8.284	2.0	5.495	—	8.889	27.2	6.2	[174]
$ZrMn_{2.2}$	$MgZn_2$	4.988	—	8.200	4.0	5.424	—	8.682	25.2	2.8	[47]
$ZrFe_2$	$MgCu_2$	7.046	—	—	0.2	7.060	—	—	1.9	3.2	[38]
ZrCo	CsCl	3.196	—	—	3.0***	3.53	10.48	4.30	22.0	2.4	[104]
ZrNi	CrB	3.258	9.941	4.094	1.0	3.28	10.04	4.24	5.3	1.7	[90]
ZrNi	CrB	3.258	9.941	4.094	3.0	3.53	10.48	4.30	20.0	2.2	[91]
$ZrMo_2$	$MgCu_2$	7.548	—	—	1.4	7.698	—	—	6.8	2.6	[38]
Zr_2Pd	$MoSi_2$	3.297	—	10.92	2.7	3.41	—	11.42	11.9	2.6	[100]
ZrAg	ZrAg	3.348	—	6.603	1.0	3.33	—	7.35	12.2	4.4	[92]
ZrTiNi	$MgZn_2$	5.147	—	8.320	3.7	5.490	—	8.909	21.7	2.2	[38]
ZrVAl	$MgZn_2$	5.297	—	8.634	2.1	5.426	—	8.869	8.1	2.0	[39]
ZrVCr	$MgCu_2$	7.281	—	—	*****	7.759	—	—	21.0	—	[64]
ZrVFe	$MgZn_2$	5.050	—	8.488	4.0	5.406	—	8.922	23.2	2.7	[39]
ZrVCo	$MgZn_2$	5.053	—	8.232	4.0	5.508	—	8.830	23.5	2.7	[39]
ZrVNi	$MgZn_2$	5.013	—	8.196	2.8	5.391	—	8.802	24.2	3.8	[39]
ZrVNi	$MgCu_2$	7.112	—	—	3.7	7.542	—	—	19.3	2.3	[39]
ZrVCu	$MgZn_2$	5.154	—	8.384	4.0	5.473	—	8.934	20.2	2.4	[39]
ZrVNb	$MgZn_2$	5.348	—	8.624	5.4	5.719	—	9.255	23.3	2.4	[39]
ZrMoCr	$MgZn_2$	5.204	—	8.523	2.4	5.415	—	8.974	12.0	2.1	[39]
ZrMoFe	$MgZn_2$	5.172	—	8.463	2.6***	5.420	—	8.826	14.5	2.7	[167]
$LaCo_2$	$MgCu_2$	7.239	—	—	3.8	5.592	5.488	7.88	26.8	3.3	[64]
LaCo$_5$	$CaCu_5$	5.109	—	3.970	3.4	8.973	5.413	4.088	11.1	2.8	[27]
LaCo$_5$	$CaCu_5$	5.109	—	3.970	4.2	9.495	5.381	3.966	11.3	2.8	[27]
LaNi	CrB	3.81	10.53	4.37	3.7***	3.982	11.94	4.873	32.2	3.8	[124]
$LaNi_5$	$CaCu_5$	5.015	—	3.987	6.0	5.426	—	4.269	18.9	2.9	[40]
$LaRu_2$	$MgCu_2$	7.702	—	—	4.0	8.42	—	—	30.7	4.4	[53]
$LaNi_4Al$	$CaCu_5$	5.066	—	4.070	4.3	5.319	—	4.225	11.5	3.1	[29]
$LaNi_4Al$	$CaCu_5$	5.066	—	4.069	4.1***	5.300	—	4.242	14.1	3.1	[133]
CeCo$_5$	$PuNi_3$	4.955	—	24.75	4.0	4.956	—	32.69	32.1	4.7	[56]
Ce_2Co_7	Ce_2Ni_7	4.930	—	24.46	6.0	4.949	—	29.69	21.8	4.7	[56]
Ce_2Co_7	Ce_2Ni_7	4.497	—	24.50	5.3	5.007	—	24.99	4.5	1.1	[42]
CeCo$_3$	$CaCu_5$	4.922	—	4.049	2.5	8.726	5.105	8.146	7.6	2.5	[27]
CeNi$_3$	CeNi$_3$	4.960	—	16.55	3.0	4.920	—	21.64	28.7	5.6	[56]
Ce_2Ni_7	Ce_2Ni_7	4.927	—	24.45	4.0	4.920	—	29.63	20.8	6.7	[56]
$CeRu_2$	$MgCu_2$	7.546	—	—	5.2***	8.383	—	—	37.1	3.8	[143]
$CeNi_4Al$	$CaCu_5$	4.943	—	4.085	3.7	5.227	—	4.186	11.5	3.4	[29]
$PrCo_2$	$MgCu_2$	7.306	—	—	4.0	15.86	—	—	28.2	3.4	[61]
$PrCo_3$	$PuNi_3$	5.068	—	24.79	1.8	5.091	—	27.57	12.2	4.2	[40]
$PrCo_4$	$PuNi_3$	5.068	—	24.79	3.7	5.380	—	27.30	24.1	3.9	[40]
Pr_2Co_7	Ce_2Ni_7	5.058	—	24.51	2.5	5.081	—	26.30	8.3	4.5	[72]
Pr_2Co_7	Ce_2Ni_7	5.058	—	24.51	5.8	5.312	—	26.04	17.1	4.0	[72]
$PrCo_5$	$CaCu_5$	5.022	—	3.989	2.8	8.837	5.261	8.110	8.1	2.5	[27]
$PrCo_5$	$CaCu_5$	5.022	—	3.989	3.6	8.868	5.341	4.083	11.1	2.7	[27]
$PrNi_4Al$	$CaCu_5$	5.023	—	4.064	3.7	5.254	—	4.203	11.3	3.2	[29]
$NdMn_{23}$	Th_6Mn_{23}	12.67	—	—	*****	13.24	—	—	14.1	—	[192]
$NdCo_2$	$MgCu_2$	7.294	—	—	3.8	7.95	—	—	29.5	3.8	[61]
$NdCo_3$	$PuNi_3$	5.055	—	24.70	1.8	5.055	—	27.40	10.9	3.7	[70]
$NdCo_4$	$PuNi_3$	5.055	—	24.70	4.0	5.357	—	27.24	23.9	3.6	[70]
Nd_2Co_7	Ce_2Ni_7	5.053	—	24.43	2.7	5.069	—	26.29	8.3	4.1	[72]
Nd_2Co_7	Ce_2Ni_7	5.053	—	24.43	6.2	5.268	—	25.92	15.3	3.3	[72]
NdCo$_5$	$CaCu_5$	5.020	—	3.977	2.7	8.819	5.247	8.092	8.1	2.5	[27]
$NdRu_2$	$MgZn_2$	5.323	—	9.004	5.5	5.88	—	9.62	30.3	3.0	[46]
$NdNi_4Al$	$CaCu_5$	5.004	—	4.067	4.0	5.229	—	4.183	11.2	2.7	[29]
$SmMn_2$	$MgZn_2$	5.111	—	8.976	3.8	5.49	—	8.86	13.9	1.9	[68]
Sm_6Mn_{23}	Th_6Mn_{23}	12.57	—	—	24	13.04	—	—	11.6	2.4	[68]
Sm_6Mn_{23}	Th_6Mn_{23}	12.56	—	—	*****	13.13	—	—	14.2	—	[192]
$SmFe_2$	$MgCu_2$	7.417	—	—	*****	8.00	—	—	29.7	—	[52]
$SmFe_3$	$PuNi_3$	5.187	—	24.91	4.2	5.40	—	27.09	17.9	2.7	[68]
$SmCo_5$	$CaCu_5$	4.995	—	3.965	2.5	8.752	5.224	8.056	7.4	2.6	[27]
$SmRu_2$	$MgZn_2$	5.298	—	8.939	4.6	5.84	—	9.53	29.5	3.5	[46]
$SmNi_4Al$	$CaCu_5$	4.980	—	4.050	3.6	5.193	—	4.155	11.1	2.8	[29]
Eu_2Ru	*	—	—	—	6.0	7.566	—	—	—	—	[115]
Eu_2Ir	*	—	—	—	5.0	7.580	—	—	—	—	[112]
$GdMn_2$	$MgCu_2$	7.724	—	—	*****	8.051	—	—	8.7	—	[42]
Gd_6Mn_{23}	Th_6Mn_{23}	12.51	—	—	*****	12.95	—	—	10.9	—	[42]
$GdFe_2$	$MgCu_2$	7.389	—	—	3.6	16.06	—	—	28.8	3.8	[185]
$GdFe_3$	$PuNi_3$	5.167	—	24.71	3.1	5.387	—	27.01	17.5	3.8	[71]
$GdCo_2$	$MgCu_2$	7.262	—	—	3.9	5.532	5.437	7.89	23.9	2.9	[61]
$GdCo_3$	$PuNi_3$	5.037	—	24.51	2.0	5.021	—	27.34	10.8	3.2	[70]
$GdCo_3$	$PuNi_3$	5.037	—	24.51	3.7	5.291	—	26.88	21.0	3.4	[70]
Gd_2Co_7	Gd_2Co_7	5.017	—	36.31	2.6	5.042	—	39.04	7.3	3.7	[72]
Gd_2Co_7	Gd_2Co_7	5.017	—	36.31	5.9	5.199	—	38.62	14.2	3.2	[72]
$GdNi_3$	$PuNi_3$	5.009	—	24.57	2.0	5.182	—	24.84	8.1	2.4	[190]
$GdNi_3$	$PuNi_3$	5.009	—	24.57	3.0	4.944	—	31.41	23.0	4.5	[188]
$GdRh_2$	$MgCu_2$	7.514	—	—	3.2	4.80	5.10	9.50	9.6	1.6	[50]
$GdNi_4Al$	$CaCu_5$	4.969	—	4.048	3.5	5.169	—	4.142	11.1	2.8	[29]
Th_6Mn_{23}	Th_6Mn_{23}	12.40	—	—	23	13.02	—	—	15.8	3.3	[89]
$TbFe_2$	$MgCu_2$	7.341	—	—	*****	7.97	—	—	28.0	—	[52]
$TbFe_2$	$MgCu_2$	7.315	—	—	3.6	16.10	—	—	33.3	4.5	[185]
$TbFe_3$	$PuNi_3$	5.143	—	24.64	4.2	5.355	—	26.71	17.5	2.6	[71]
$TbCo_2$	$MgCu_2$	7.211	—	—	3.3	15.48	—	—	23.6	3.4	[61]
$TbCo_3$	$PuNi_3$	5.016	—	24.43	2.0	5.005	—	26.80	9.2	2.7	[70]
$TbCo_3$	$PuNi_3$	5.016	—	24.43	3.8	5.262	—	28.85	20.9	3.3	[70]
Tb_2Co_7	Gd_2Co_7	5.007	—	36.27	2.7	5.041	—	38.96	7.6	3.7	[72]
Tb_2Co_7	Gd_2Co_7	5.007	—	36.27	6.6	5.175	—	38.48	13.3	2.7	[72]
$TbNi_2$	$MgCu_2$	7.154	—	—	3.6	7.624	—	—	21.0	2.7	[185]
$TbNi_3$	$PuNi_3$	4.979	—	24.48	4.2	5.302	—	26.78	24.0	3.3	[190]
$TbNi_4Al$	$CaCu_5$	4.941	—	4.037	3.2	5.134	—	4.131	11.1	2.8	[29]
$DyMn_2$	$MgCu_2$	7.564	—	—	3.4	8.27	—	—	15.4	2.4	[65]
Dy_6Mn_{23}	Th_6Mn_{23}	12.36	—	—	23	12.90	—	—	13.6	2.8	[89]
$DyFe_2$	$MgCu_2$	7.309	—	—	3.4	7.94	—	—	28.2	4.0	[65]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	1.8	5.26	—	25.54	10.0	3.4	[75]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	2.5	5.34	—	25.80	14.5	3.6	[75]
$DyFe_3$	$PuNi_3$	5.130	—	24.52	3.0	5.31	—	26.59	16.2	3.3	[71]
$DyFe_3$	$PuNi_3$	5.116	—	24.55	4.2	5.36	—	26.46	18.0	2.7	[75]
$DyCo_2$	$MgCu_2$	7.187	—	—	3.4	7.724	—	—	24.0	3.3	[65]
$DyCo_2$	$MgCu_2$	7.191	—	—	3.7	7.759	—	—	25.6	3.2	[185]
$DyCo_3$	$PuNi_3$	5.007	—	24.27	2.1	4.992	—	26.61	9.0	2.5	[70]
$DyCo_3$	$PuNi_3$	5.007	—	24.27	3.7	5.233	—	26.66	20.0	3.2	[70]
Dy_2Co_7	Gd_2Co_7	4.988	—	36.15	2.6	4.984	—	38.70	6.9	3.4	[72]
Dy_2Co_7	Gd_2Co_7	4.988	—	36.15	6.4	5.169	—	38.31	13.8	2.8	[72]
$DyNi_2$	$MgCu_2$	7.149	—	—	2.0	7.551	—	—	17.8	4.1	[65]
$DyNi_2$	$MgCu_2$	7.150	—	—	3.5	7.58	—	—	19.2	2.5	[61]
$DyNi_3$	$PuNi_3$	4.980	—	24.44	2.2	5.039	—	26.67	11.9	3.1	[188]
$DyNi_3$	$PuNi_3$	4.980	—	24.44	3.4	5.280	—	26.74	23.0	3.9	[188]
$DyNi_4Al$	$CaCu_5$	4.928	—	4.038	*****	5.107	—	4.120	11.0	—	[29]
$HoFe_2$	$MgCu_2$	7.305	—	—	*****	7.73	—	—	15.5	—	[52]
$HoFe_2$	$MgCu_2$	7.291	—	—	3.6	15.82	—	—	27.7	3.7	[61]
$HoFe_3$	$PuNi_3$	5.177	—	24.48	3.6	5.316	—	26.39	16.4	2.8	[71]
Ho_6Fe_{23}	Th_6Mn_{23}	12.03	—	—	16	12.40	—	—	9.5	1.7	[191]
$HoCo_2$	$MgCu_2$	7.158	—	—	3.6	7.68	—	—	23.5	3.0	[61]
$HoCo_3$	$PuNi_3$	4.985	—	24.22	2.0	4.990	—	26.12	8.1	2.3	[70]
$HoCo_3$	$PuNi_3$	4.985	—	24.22	3.3	5.233	—	26.33	19.8	3.0	[70]
$HoNi_2$	$MgCu_2$	7.128	—	—	3.6	7.49	—	—	16.0	2.0	[61]
$HoNi_3$	$PuNi_3$	4.953	—	24.21	1.8***	4.991	—	26.12	9.6	3.0	[178]
$HoNi_3$	$PuNi_3$	4.963	—	24.28	3.6	5.305	—	26.70	20.4	4.1	[188]
$HoRu_2$	$MgZn_2$	5.244	—	8.810	4.2	5.65	—	9.33	22.9	2.9	[46]
$HoNi_4Al$	$CaCu_5$	4.919	—	4.037	*****	5.105	—	4.128	11.0	2.6	[29]
$ErMn_2$	$MgZn_2$	5.307	—	8.702	4.0	5.640	—	9.35	21.4	2.8	[41]
$ErFe_2$	$MgZn_2$	5.307	—	8.702	4.6	5.810	—	9.53	31.3	3.6	[41]
$ErFe_2$	$MgCu_2$	7.260	—	—	*****	7.94	—	—	29.3	—	[52]
$ErFe_2$	$MgCu_2$	7.269	—	—	3.0	15.73	—	—	26.6	4.3	[61]
$ErFe_2$	$MgCu_2$	7.269	—	—	3.9	7.82	—	—	25.0	3.1	[58]
$ErFe_2$******	$MgCu_2$	7.260	—	—	4.0	7.828	—	—	25.0	2.8	[66]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	1.5	5.20	—	25.47	7.1	2.9	[74]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	2.7	5.26	—	25.68	11.8	2.7	[74]
$ErFe_3$	$PuNi_3$	5.104	—	24.56	2.7	5.267	—	26.16	13.4	3.0	[71]
$ErFe_3$	$PuNi_3$	5.096	—	24.48	4.0	5.30	—	26.40	16.7	2.5	[74]
Er_6Fe_{23}	Th_6Mn_{23}	12.00	—	—	14	12.13	—	12.60	7.3	2.2	[191]
ErCo$_5$	$MgCu_2$	7.139	—	—	3.5	7.61	—	—	21.1	2.7	[61]

Table 3 (cont'd).

IMC	Structure type	Lattice parameters, A			H: $M_xM'_y$	Lattice parameters, A			$\Delta V/V_0$, %	ΔV/atoms of H, A^3	Refs.
		a	*b*	*c*		*a*	*b*	*c*			
$ErCo_3$	$PuNi_3$	4.977	—	24.26	1.8	4.981	—	25.83	6.6	2.1	[70]
$ErCo_3$	$PuNi_3$	4.977	—	24.26	3.6	5.223	—	26.27	19.3	3.1	[70]
$ErNi_2$	$MgCu_2$	7.108	—	—	3.1***	7.43	—	—	14.2	2.1	[40]
$ErNi_2$	$MgCu_2$	7.108	—	—	3.5	7.68	—	—	26.1	3.4	[61]
$ErNi_3$	$PuNi_3$	4.951	—	24.27	1.9	4.980	—	25.85	7.8	2.3	[190]
$ErRu_2$	$MgZn_2$	5.227	—	8.780	3.6	5.64	—	9.31	23.5	3.4	[46]
$ErNi_4Al$	$CaCu_5$	4.910	—	4.033	*****	5.096	—	4.122	11.0	—	[29]
$TmFe_2$	$MgCu_2$	7.252	—	—	3.0	15.44	—	—	20.6	3.3	[61]
$TmCo_2$	$MgCu_2$	7.122	—	—	3.7	7.600	—	—	21.5	2.6	[185]
$TmNi_2$	$MgCu_2$	7.095	—	—	3.6	7.52	—	—	19.1	2.4	[40]
$TmNi_3$	$PuNi_3$	4.935	—	24.26	2.0	4.983	—	25.85	8.6	2.4	[190]
$TmNi_4Al$	$CaCu_5$	4.900	—	4.026	*****	5.078	—	4.121	11.0	—	[29]
Yb_2Ru	*	—	—	—	6.0	7.248	—	—	—	—	[107]
$LuMn_2$	$MgZn_2$	5.227	—	8.537	*****	5.745	—	9.458	34.1	—	[42]
Lu_6Mn_{23}	Th_6Mn_{23}	12.21	—	—	*****	12.46	—	—	6.3	—	[42]
$LuFe_2$	$MgCu_2$	7.199	—	—	3.0	7.691	—	—	21.9	3.4	[185]
$LuCo_2$	$MgCu_2$	7.082	—	—	0.7	7.110	—	—	1.2	0.7	[185]
$LuCo_2$	$MgCu_2$	7.082	—	—	3.2	7.553	—	—	21.3	3.0	[185]
$LuNi_2$	$MgCu_2$	7.084	—	—	2.5	7.44	—	—	9.1	1.7	[40]
HfV_2	$MgCu_2$	7.37	—	—	4.0***	7.78	—	—	12.2	2.8	[144]
Hf_2Mn	Ti_2Ni	11.886	—	—	3.0	12.60	—	—	19.1	3.3	[82]
Hf_2Fe	Ti_2Ni	12.038	—	—	3.1	12.87	—	—	22.2	3.9	[82]
Hf_2Co	Ti_2Ni	12.071	—	—	3.6	12.74	—	—	17.6	2.7	[82]
HfCo	CsCl	3.164	—	—	3.2	3.485	10.35	4.267	21.4	2.1	[82]
Hf_2Ni	$CuAl_2$	6.395	—	5.240	3.1	6.740	—	5.608	18.9	3.3	[82]
HfNi	CrB	3.218	9.788	4.117	3.2	3.464	10.35	4.253	17.6	1.8	[82]
Hf_2Cu	$MoSi_2$	3.164	—	11.15	2.9	6.35	6.94	11.71	15.6	3.0	[100]
Hf_2Pd	$MoSi_2$	3.251	—	11.06	1.9	3.28	—	11.61	6.8	2.1	[100]
Hf_2Rh	Ti_2Ni	12.271	—	—	2.2	12.76	—	—	12.4	3.3	[82]
TaV_2	$MgCu_2$	7.14	—	—	1.7	7.34	—	—	8.6	2.3	[63]
Th_2Al	$CuAl_2$	7.616	—	5.861	4.0***	7.629	—	6.517	11.6	2.5	[165]
$ThTi_2$	*	—	—	—	6.0	9.124	—	—	—	—	[113]
$ThMn_2$	$MgZn_2$	5.478	—	8.941	*****	6.110	—	9.861	36.9	—	[42]
Th_6Mn_{23}	Th_6Mn_{23}	12.52	—	—	30	13.26	—	—	18.8	3.1	[57]
Th_7Fe_3	Th_7Fe_3	9.823	—	6.211	14.2	10.8	—	6.80	32.3	5.9	[93]
$ThZr_2$	*	—	—	—	7.0	6.176	—	10.085	—	—	[113]
ThNiAl	Fe_2P	7.078	—	4.053	3.0	7.340	—	4.228	12.2	2.4	[198]
$ThNi_2Al_2$	$CaCu_5$	5.127	—	4.120	2.7	5.217	—	4.183	5.0	1.8	[28]
UNiAl	Fe_2P	6.739	—	4.038	2.7	7.223	—	3.953	12.5	2.4	[198]

*The hydride phase is formed by high-temperature synthesis from two binary hydrides or from metal M′ and the hydride of metal M in a hydrogen atmosphere.

**β = 93.2°.

***Data for deuterated specimens.

****β = 97.0°.

*****Composition of hydride phase not given in original work.

******α = 93.5°.

The results presented suggest that the minimum radius for the hydrogen atom in metal hydrides is close to 0.2 Å. However, like other results suggesting that hydrogen can have an effective radius less than 0.2 Å (0.11 Å in the $LiPtD_{0.66}$ structure[160,161]), this requires careful experimental verification by carrying out more detailed and systematic structural researches.

The minimum H–H distances are either similar to or a little greater than the analogous distances in binary hydride structures. There is one exception, the Th_2AlD_3 structure[165], in which the presence of short H–H distances of length 1.66 Å was confirmed by n.m.r.

While this review was in the press a whole series of new papers on the structural chemistry of IMC hydrides[166–202] was published. The results of the most important of them are discussed briefly below.

The range of subjects for neutron-diffraction investigation has been broadened mainly through the study of new representatives of hydride phases formed on the basis of IMC's with structures belonging to the homologous series MM'_5–MM'_2 ($CaCu_5$ type—Laves phases). The deuterides $ZrVFeD_{3.6}$, $ZrVCuD_{4.0}$, and $ZrVNbD_{5.4}$ [166] based on IMC's with the $MgZn_2$ type structure are particularly interesting as the stoichiometric composition of the last of them is the maximum for hydrides based on the Laves phases. The tendency for preferential occupation of the $[hM_2M'_2]$ holes in the metal lattice was found to be maintained also in the structures of hydride phases richer in hydrogen than $ZrMoFeD_{2.6}$[138,139,167] and $ZrMn_2D_{3.0}$.[140] Thus in the $ZrVFeD_{3.6}$ and $ZrVNbD_{5.4}$ structures the $[hM_2M'_2]$ holes are occupied by up to 97% of the hydrogen atoms, and in the $ZrVCuD_{4.0}$ structure 89%. In addition a small number of hydrogen atoms are in $[hZrM'_3]$ holes, and for $ZrVCuD_{4.0}$ filling of the $[hM'_4]$ holes is also typical.

A comparison of all five ZrM'_2D_x structures based on IMC's with the $MgZn_2$ type structure which have been studied up to now shows that an equally probable distribution of hydrogen atoms in the $[hZr_2M'_2]$ holes does not occur in any of the structures. It is of interest that all the structures with $D/ZrM'_2 \leq 4.0$ are related to each other and may be regarded as derivatives of $ZrMoFeD_{2.6}$ which is the "poorest" in hydrogen: when the D/ZrM'_2 ratio exceeds 2.6, in addition to the two types of $[hZr_2M'_2]$ hole filled in $ZrMoFeD_{2.6}$, hydrogen atoms enter into two more types of hole in the metal sublattice different for each particular structure. The way in which the hydrogen atoms are distributed in the holes in the $ZrVNbD_{5.4}$ structure differs in principle from that in the other structures. There is a redistribution of the hydrogen atoms between two groups of $[hZr_2M'_2]$ holes in six-fold equivalent positions, as a result of which not only can the limiting composition $MM'_2H_{4.5}$ for the alternative model be exceeded without substantial distortion of the $MgZn_2$ type structure, but also the maximum stoichiometric composition $MM'_2H_{6-6.5}$ can be attained.

Returning to the results given in the main part of the review, we may conclude that an almost complete analogy exists between the structure of the hydride phases $MM'_2H(D)_x$ based on IMC's with $MgCu_2$ and $MgZn_2$ type structures: at low hydrogen concentrations only the $[hM_2M'_2]$ holes are filled, and on increasing the hydrogen content the preference for filling these holes is retained, but hydrogen atoms are also inserted into holes with a smaller content of metal M, in the $[hMM'_3]$ holes in the first place.

Several recent publications[168–170] are devoted to hydrides based on MM'_5 compounds with the $CaCu_5$ type structure.

The structure of the mixed oxyhydride phase $Ti_4Fe_2.OD_{2.25}$ [171] (the parent IMC Ti_2Fe crystallises in the Ti_2Ni type only in the presence of oxygen) is of undoubted interest. The presence of chemisorbed oxygen in the lattice must indicate fairly definitely the choice of positions for the introduction of hydrogen atoms. As with the shortest H–H interatomic distances characterising the "blocking radius" of neighbouring holes, an analogous value can also be determined for the O–H(D) contacts. The experimentally determined value d_{O-D} = 1.68 Å for the $Ti_4.Fe_2OD_{2.25}$ structure, as expected, substantially exceeds the value 0.96 Å typical of an O–H covalent bond in the water molecule, and lies in the typical range for the length of O...H hydrogen bonds, which undoubtedly indicates a definite interaction between the oxygen and hydrogen atoms.

Three types of hydrogen atom in the structure occupy two different types of hole, their coordination polyhedra being the octahedron $[D^{(1)}Ti_6]$ and the tetrahedra $[D^{(2)}.Ti_3Fe]$ and $[D^{(3)}Ti_3Fe]$, as atoms $D^{(2)}$ and $D^{(3)}$ occupy the same type of hole. The crystallographic positions, which these atoms can occupy inside a specific hole, are within a sphere of diameter ~0.3 Å.

A characteristic feature of IMC hydrides is that they are, as a rule, non-stoichiometric and that in their structures there is a statistical distribution of hydrogen atoms in crystallographic positions, with the number of positions substantially exceeding the number of inserted atoms. When the temperature is reduced, owing to the non-zero configurational entropy, phase transitions of the order-disorder type[172,173] must take place, leading to removal of the "degeneracy" of the equivalent holes—some of them are filled in an ordered way, and the remainder become vacant. In addition to $ZrV_2D_{3.7}$ [145] and $HfV_2D_{4.0}$ [144] discussed above, such transitions were observed as the temperature is lowered in Sr_2IrD_5.[174] The order-disorder phase transition in the last case is accompanied by a lowering of the lattice symmetry from cubic to tetragonal and a reduction in the deuterium atom occupation factor of each of five Sr_4Ir pyramids ($n = 0.70$), while the occupation factor of the remaining [hSr_4Ir] holes is close to the possible limit ($n = 0.96$). A similar phase transition on reducing the temperature also takes place in a hydride phase based on the IMC Y_6Mn_{23} [175]—here the lattice symmetry is lowered from cubic (space group $Fm3m$) to tetragonal ($P4_2/mnm$).

X-Ray diffraction studies, like neutron-diffraction work, have been carried out mainly for hydride phases based on IMC's with Laves phase and $CaCu_5$ type structures. A study of the process of hydrogenation and subsequent dehydrogenation of $CaNi_5$, carried out under conditions of equilibrium saturation of specimens with hydrogen directly in the course of the X-ray diffraction experiment[176], showed the presence of three hydride phases, α' ($CaNi_5H_{0.8-1.2}$), β ($CaNi_5H_{4.5-5.6}$), and γ ($CaNi_5H_{6+x}$), whose symmetry changes from hexagonal to orthorhombic and again to hexagonal (trigonal) as the hydrogen content in the hydride is increased. Data on the existence of $CaNi_5H_5$ with an orthorhombic structure had been obtained independently and previously[177].

For hydrides based on the alloys $LaNi_{5-x}Fe_x$ [178] the hexagonal symmetry of the IMC is retained.

Among Laves phase hydrides studied in the most detail are alloys, whose composition corresponds to the quasi-binary section MM'_2–MM''_2, namely $Zr(Cr, Fe)_2$, $Zr(Cr, Co)_2$,[179] $Tb(Co, Fe)_2$, $Dy(Co, Fe)_2$,[180] $Zr(Mn, Fe)$,[181] $Zr(V, Fe)_2$, $Zr(V, Cr)_2$,[182] $Ti(Be, Cu)_2$,[183] $Ho(Co, Fe)_2$ and $Er(Co, Fe)_2$.[184] The systematic investigation of the hydrides MM'_2H_x (M = lanthanide, M' = Fe, Co, Ni) has also been continued[185–187]. It was found that the original symmetry of the unit cells of the IMC structures is retained and their volume increases by $\Delta V \sim 2.5$ Å^3 for each H atom.

Systematic researches on the hydrides MM'_3H_x (M = Y, Gd, Dy, Ho; M' = Ni, Co),[188–190] based on IMC's with the $PuNi_3$ type structure, and also $M_6M'_{23}H_x$ (M = Y, Sm, Gd, Ho, Er; M' = Mn, Fe) [191,192] (parent IMC's of the Th_6Mn_{23} type) have been continued. The results confirmed earlier conclusions as to the crystallographic characteristics of the hydride phases in the related systems MM'_3–H_2 [70–72] and $M_6M'_{23}$–H_2.[87–89] Similar conclusions can be drawn for the hydrides based on the alloys $TiFe_{1-x}M'_x$, where M' = Al, Cr, Mn, Co, Ni.[193,194] The structure and properties of hydrides based on IMC's of titanium have been investigated[195,196]. A re-examination of the structural phase transitions in Mg_2NiH_4 [197] is in agreement with earlier results[102,103].

The reaction of the compounds UNiAl and ThNiAl with hydrogen has been investigated[198]. These compounds belong to the Fe_2P structure type, which can be regarded as a packing of trigonal prisms and is in this sense similar to one of the structure types whose reaction with hydrogen was studied previously, namely CrB. The hexagonal unit cells of the parent intermetallic compounds behave differently on hydrogenation: in ThNiAl the expansion is practically isotropic and fairly small ($\Delta a/a_0 \sim \Delta c/c_0 \sim 0.04$), whereas the UNiAl structure is "compressed" in the z axis direction and substantially expanded in the basal plane ($\Delta a/a_0 \sim 0.07$).

In addition to neutron and X-ray diffraction experimental researches, work has been published in which, by identifying all possible types of hole in the metal matrix, the most probable models for the structure of hydride phases based on IMC's crystallising in the Th_6Mn_{23} [199] and CrB types[200] have been considered. The most probable models for the structure of the hydrides $MM'H_x$ (CrB parent type) and MM'_3H_x ($PuNi_3$ parent type) have been discussed in connection with elucidation of the structure of $HoNi_3D_{1.8}$.[202]

There is also a review in the field of binary hydride structural chemistry[203] giving results on the synthesis of transition-metal hydrides by direct reaction of the metals with hydrogen at high hydrogen pressures and on their properties. This synthetic method has recently permitted the range of "hydrogenated" metals to be extended to gold, which forms a hydride of approximate composition $AuH_{0.4}$ with an orthorhombic structure[204].

Thus, in the structures of complex metal hydrides studied up till now the hydrogen atoms most frequently have a c.n. of 4 or 6 with tetrahedral or octahedral coordination, more rarely a c.n. of 3 or 5, but linear coordination is observed only for two structures. In most cases there is no reorganisation of the IMC structure when hydrogen atoms are introduced into their lattices.

Of the different types of hole in the metal lattice, those filled first in the hydrides are those surrounded by the greatest number of atoms of the metal M. This rule is general for metal hydride structures and can be explained by the simultaneous effect of a number of factors: (1) the activity of metal M on reaction with hydrogen; (2) the greatest effective size of these holes of all those present in the metal lattice; (3) the M–M distances in the periphery of the holes occupied by hydrogen atoms exceed the sum of the corresponding metal radii, so that these holes are the most easily deformed when the hydride phases are formed.

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