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Synthesis and structure of new metal hydrides

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Abstract

The synthesis and structural characterization by X-ray and neutron diffraction experiments of ternary metal hydrides $A_xM_yH_z$, in which A is an alkali metal or alkaline-earth metal and M is a transition metal, led to the discovery of anionic complex groups of the form $[MH_z]^{n-}$. Although there are obvious structural similarities to the corresponding halides and oxides, the dynamic properties of the hydride ligand are somewhat unusual and are responsible for the numerous phase transformations. Transitions from salt-like to metallic behaviour within this range of compounds lead us to expect interesting physical properties and applications.

Keywords: Metal hydrides; Alkali metal; Alkaline-earth metal; Structure; Metallic behaviour

1. Introduction

Metal hydrides have been of steadily increasing importance for a long time due to their technical applications. The original interest in the area of their practical employment centred on the insertion of hydrogen into palladium and nickel which relates directly to the catalysis of a number of chemical processes. The use of hydrides of transition-metal alloys in modern applications was subsequently developed and examples in this area include the compounds $FeTiH_2$ and $LaNi_5H_6$ which can be used for the purpose of storing hydrogen. More recently, the applications of metal hydrides have been widened to include their use in accumulator units. In general it has been found that the magnetic or electrical properties and also the superconductivity of intermetallic compounds can be strongly influenced by the inclusion of interstitial hydrogen atoms. Examples of this type include palladium and the Ln_2Fe_{17} phases ($Ln \hat{=}$ Lanthanide). Simultaneously with the development of the hydrides of the transition metals and of their alloys relating to practical applications, new uses were also found for main-group metal hydrides. A major case in this regard is $LiAlH_4$ which provides the possibility of selective hydrogenation.

The original research into the field of metal–hydrogen compounds was largely orientated towards their practical uses and, consequently, a considerable amount of work has been published concerning the binary and ternary metal hydrides which are of import in this regard whilst the hydrides of elements from other regions of the periodic system were almost completely neglected. Only in recent times has basic research been undertaken in which the application of the resulting hydride has not been the foremost consideration.

In the following a section of research results will be reported that concern these latter hydrides and which are exclusively limited to such hydrides as have been synthesized and investigated at the Institute of Inorganic Chemistry of the Technische Hochschule Aachen. The main concept that lay behind this research was that, since binary metal hydrides can be broadly assigned as salt-like, covalent or metallic compounds, one of the three possible combinations of these binary hydrides could lead to a class of ternary hydrides of the general composition $A_xM_yH_z$. The composites of these compounds include one metal (A) that originates from the area of salt-like hydrides whilst the other (M) stems from the area of metallic hydrides. This group of compounds can, depending upon the choice of the metals A and M, exhibit more salt-like or more metallic properties. Little was known in this region when the research was initiated and the programme appeared an attractive prospect.

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2. General remarks on the synthesis and structure determination

One reason for our incomplete knowledge about the class of ternary metal hydrides $A_xM_yH_z$ where $A \hat{=}$ alkali metal or alkaline-earth metal and $M \hat{=}$ transition metal lies with the fact that their synthesis is, in general, more laborious than for other metal–nonmetal compounds. This is largely because the hydrides are often extremely sensitive towards air and moisture. However, the difficulties that occur in the synthesis and subsequent handling of these hydrides can be avoided by working entirely within closed apparatus systems [1,2]. Methods of synthesizing ternary hydrides $A_xM_yH_z$ include both molecular reactions in solvents and solid-state reactions in gaseous atmospheres. In the field of solid-state reactions referred to, one either employs an intermetallic compound into which the hydrogen is directly inserted using suitable pressures and temperatures, or alternatively allows a hydride of an alkali metal or alkaline-earth metal to react with a transition metal in an atmosphere of hydrogen.

A second reason why the information currently known about metal hydrides is so meagre has to do with the difficulty involved in the determination of the hydrogen sites in the matrix of metal atoms. In X-ray investigations this problem can usually only be resolved, if at all, with insufficient accuracy. The customary structure solution by means of single crystals is seldom possible because single crystals of metal hydrides are difficult to grow. Consequently, structures of metal hydrides are usually determined using a combination of X-ray and neutron diffraction experiments on powdered samples, in which modern high-resolution methods are of increasing importance [3]. With respect to the neutron diffraction experiments it is necessary to use the deuterium compounds because the scattering by ^1H atoms is not sufficiently coherent.

3. Alkali-metal platinum hydrides

In the Li–Pt–H system, it has been observed that the intermetallic phase LiPt, whose structure corresponds to an ordered, hexagonal close packing of metal atoms, can incorporate hydrogen atoms in tetrahedral holes within the lattice. The hydrogen uptake is reversible, and the limiting composition corresponds to the $LiPtH_{0.66}$ formula [4].

In the case of sodium, however, a complex, colourless hydride of the composition Na_2PtH_4 has been prepared [1]. Investigation of its structure revealed that it belongs to a hitherto unknown tetragonal structure type in which the characteristic structural units are planar $[PtH_4]^{2-}$ groups (Fig. 1(a)). The structure is closely related to that of K_2PtCl_4. Above 573 K, Na_2PtH_4 adopts a further modification in which the atomic arrangement conforms to the K_2PtCl_6-type structure [2] but with the chlorine sites statistically occupied by hydrogen ligands with an occupancy factor of 2/3 (Fig. 1(b)).

Similarly, in the K–Pt–H system, a colourless hydride exists with the composition K_2PtH_4 [5,6] whose structure at room temperature belongs to the K_2PtCl_6-type (Fig. 2(b)). Neutron diffraction measurements on the deuterated compound enabled a complete structure determination and showed that the deuterium sites have an occupancy factor of 2/3. At 195 K, K_2PtH_4 undergoes a reversible phase transition. In this low temperature modification, the four hydrogen ligands form the expected square-planar coordination

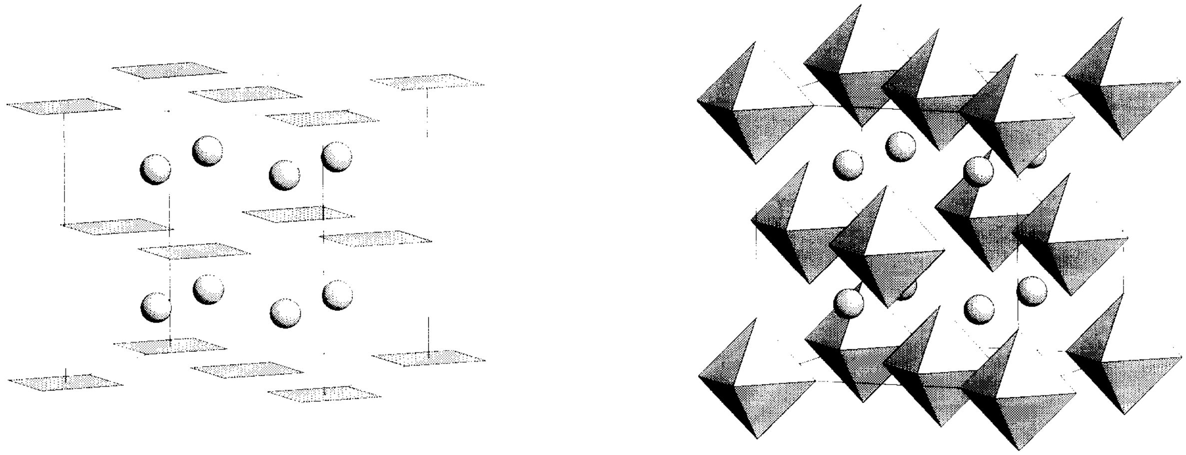

Fig. 1. The phase transformation in Na_2PtD_4: (a) low temperature form, showing the positions of the sodium atoms and the planar $[PtD_4]^{2-}$ groups; (b) high temperature form, in which hydrogen atoms occupy the vertices of the octahedra to the extent of 2/3 on average. The structure of the low temperature form of Na_2PtD_4 is shown from the same viewpoint as the high temperature form, although it may be decribed by a tetragonal unit cell that is half as large and that has the following cell parameters: $a_{tetr} = a_{cub}/\sqrt{2}$ and $c_{tetr} = a_{cub}$

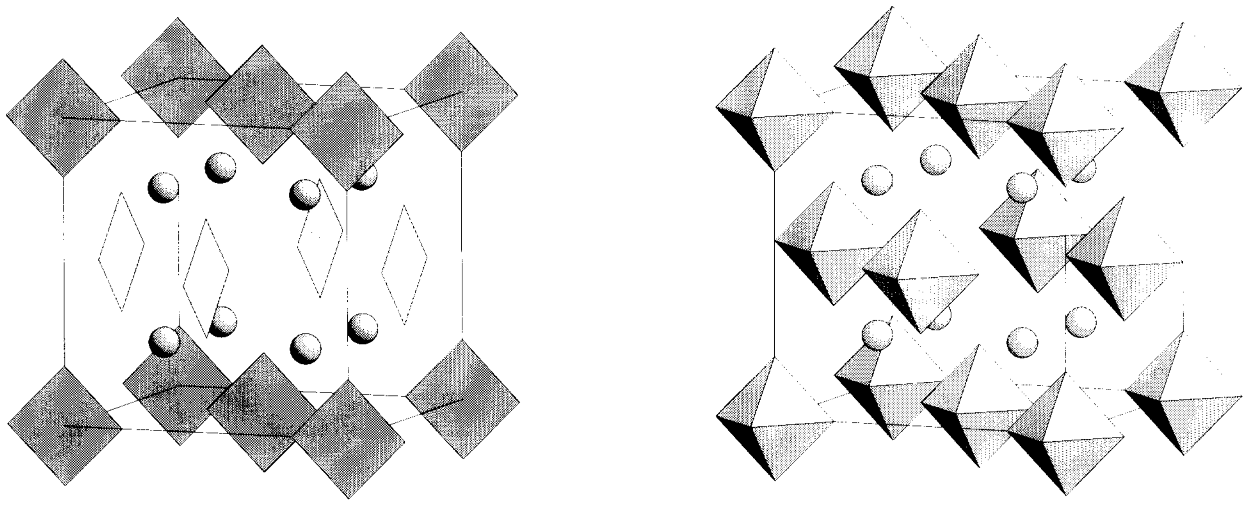

Fig. 2. The phase transformation in K_2PtD_4: (a) low temperature form, showing the positions of the potassium atoms and the planar $[PtD_4]^{2-}$ groups; (b) high temperature form, in which hydrogen atoms occupy the vertices of the octahedra to the extent of 2/3 on average. The structure of the low temperature form of K_2PtD_4 is shown from the same viewpoint as the high temperature form, although it may be described by a tetragonal unit cell that is half as large and that has the following cell parameters: $a_{\mathrm{tetr}} = a_{\mathrm{cub}}/\sqrt{2}$ and $c_{\mathrm{tetr}} = a_{\mathrm{cub}}$

around the d^8 Pt(II)ions (Fig. 2(a)). The results of ^{2}H NMR measurements on a powdered sample of K_2PtD_4 yielded a first insight into the dynamic properties of the hydrogen ligands [7] (see Fig. 3). Below 180 K the spectral width is virtually constant and the spin-lattice relaxation time is of the order of minutes, suggesting a rigid lattice behaviour. Between 180 and 210 K, the shape of the signal alters drastically. This can be explained in terms of a model in which the $[PtD_4]$ squares undergo rotational jumps about the C_4 axis of the plane. Above the phase transition temperature, an octahedral coordination of the platinum atoms is achieved via fast rotational jumps of the four deuterium atoms of each square-planar unit around the fourfold axes. The value of T_1, at 292 K is 40 ms.

The compounds Rb_2PtH_4 and Cs_2PtH_4 both crystallize in the two modifications isotypic to K_2PtH_4 [6].

For the preparation of K_2PtH_4, Rb_2PtH_4 and

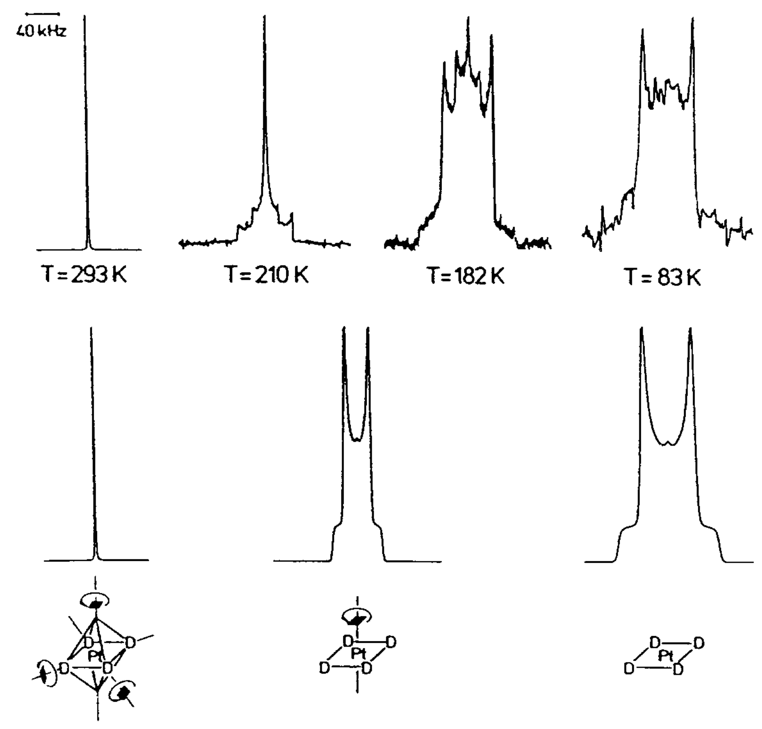

Fig. 3. ^{2}H NMR spectra of K_2PtD_4 at different temperatures. Top: observed spectra. Bottom: calculated spectra for the dynamic processes described in the text.

Cs_2PtH_4, it was found necessary to use an excess of the respective alkali-metal hydride. Closer investigation revealed this to be due to the initial formation of hydrides containing a higher proportion of the alkali metal which were then converted into the A_2PtH_4 compounds at higher temperature. These novel initial products have the formula A_3PtH_5 and adopt the atomic arrangement shown in Fig. 4 [8]. The tetragonal structure contains two types of hydrogen atoms. The first type forms the characteristic $[PtH_4]^{2-}$ units whereas the second type is octahedrally coordinated by six alkali-metal atoms, as found in the binary alkali-metal hydrides. The well-known structural similarity between complex hydrides and their corresponding halides can also be observed here, since the ternary fluorides A_3PdF_5 ($A \hat{=} Rb$ or Cs) crystallize in the same structural type [9]. However, as has commonly been found, the hydrides differ from the halides in that the hydride ligand possesses a high degree of mobility around the coordination sphere of the transition-metal atom. For example, studies of the structures of Rb_3PtH_5 and Cs_3PtH_5 and the corresponding deuterides as a function of temperature revealed that their structures transform from tetragonal to cubic at higher temperatures [8]. Evidently, the $[PtH_4]^{2-}$ groups display a dynamic behaviour in this case in which their average configuration maintains the cubic symmetry and, consequently, induces a high symmetry in the total atomic arrangement (see Fig. 5).

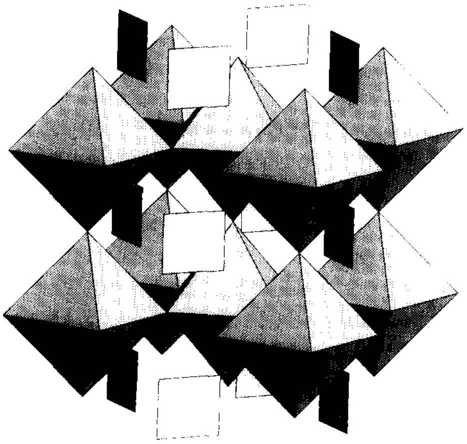

Fig. 4. Atomic arrangement of K_3PtD_5, showing the vertex-shared potassium octahedra, which have hydride ions at their centres, and the planar $[PtD_4]^{2-}$ groups.

4. Alkali-metal palladium hydrides

In the area of alkali metal–palladium–hydrogen compounds, the hydride Na_2PdH_2 was simultaneously prepared in Aachen and Stockholm [10]. Its crystal structure is shown in Fig. 6 and the complex anions in this case consist of linear $[PdH_2]^{2-}$ groups. Assuming that the palladium atoms are present in the zero oxidation state, the ligand arrangement in this compound corresponds to that found in analogous Ag(I) complexes. Although no known halide exists with an isotypic crystal structure, there is an oxide, Na_2HgO_2, in which the central atom has the same d^{10} configuration [11]. In the Li–Pd–H system, the isostructural compound Li_2PdH_2 has been reported [12]. Hydride phases containing lower proportions of lithium also exist, as in the case of the platinum phases referred to earlier, and their structures can be regarded as consist-

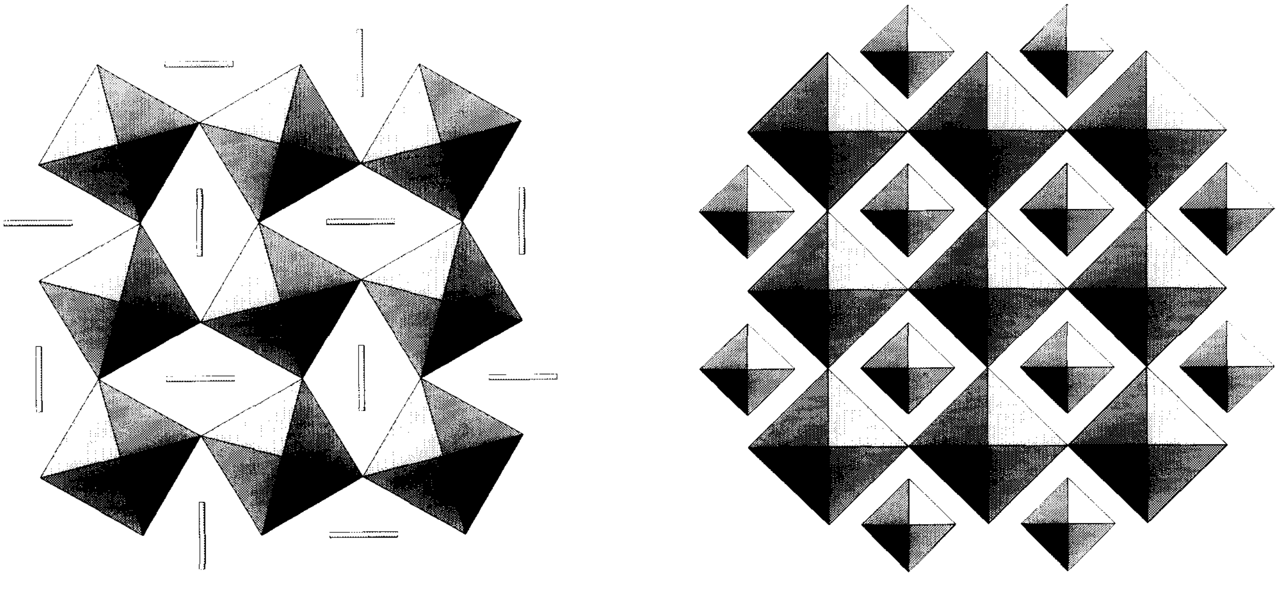

Fig. 5. Arrangement of the potassium octahedra and of the $[PtD_4]^{2-}$ groups in (a) the tetragonal, low temperature modification of K_3PtD_5 and (b) its cubic, high temperature modification.

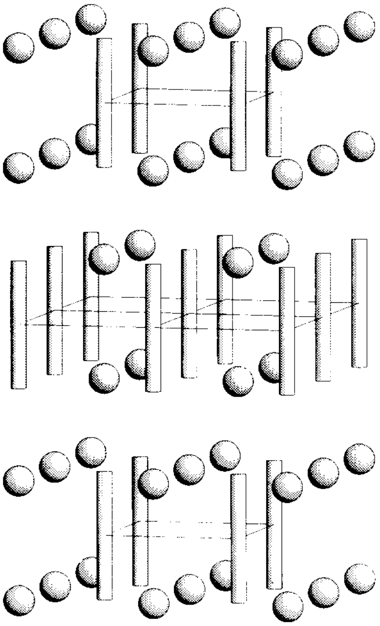

Fig. 6. Crystal structure of Na_2PdD_2, showing the positions of the sodium atoms and the linear $[PdD_2]^{2-}$ groups.

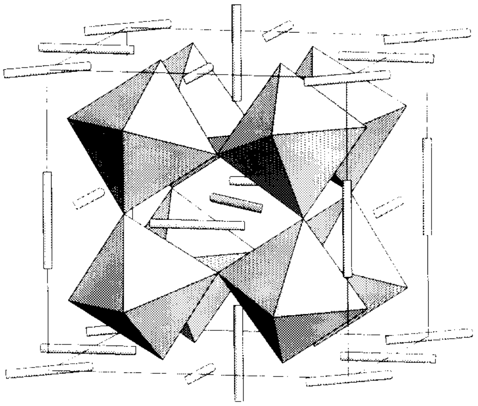

Fig. 7. Atomic arrangement of the tetragonal, low temperature modification of K_3PdD_3, showing the vertex-shared potassium octahedra, which have hydride ions at their centres, and the linear $[PdD_2]^{2-}$ groups.

ing of an ordered array of metal atoms in which the hydrogen atoms occupy octahedral sites [13].

In the K–Pd–H system, a yellow compound with the composition K_3PdH_3 has been synthesized [14]. Its structure is related to that of K_3PtH_5 and, again, contains two types of hydrogen atom which are bonded differently. One type occurs in $[PdH_2]^{2-}$ groups that are characteristic of Pd^0 and the second type is octahedrally coordinated by potassium atoms, as observed in potassium hydride (see Fig. 7). Owing to the space occupied by the linear groups, the potassium octahedra are tilted relative to each other as is shown in Fig. 8. In the related structure of K_3PtH_5, the potassium octahedra are only slightly twisted relative to each other (compare Fig. 5). A phase transition at 500 K has been observed for K_3PdH_3 and this, again, appears to result from dynamic behaviour of the hydrogen atoms in the complex units such that the average ligand environment around the palladium atoms is of cubic symmetry. The tilting of the potassium octahedra thus disappears above 500 K (Fig. 8) and this results in a cubic unit cell whose volume is 1/8 that of the tetragonal cell in the low temperature form. The arrangement of the potassium and palladium atoms in the high temperature modification corresponds to that in the $AuCu_3$ structure and is identical with the metal atom arrangement in the corresponding modification of K_3PtH_5.

The discovery that, under comparable synthesis conditions, platinum compounds can be prepared containing platinum in the +II oxidation state and palladium compounds with palladium in the 0 oxidation state, confirms the general observation that the relative stability of the higher oxidation states increases with increasing atomic mass in the transition-metal groups. Varying the experimental conditions such that higher hydrogen pressures are used in the syntheses resulted in an additional oxidative strength being observed. By these means, Pd(II)compounds were prepared whose structural characterization via neutron diffraction experiments indicated that the hydrides A_2PdH_4 [15,16] and A_3PdH_5 [17] ($A \triangleq K$, Rb or Cs) possess identical atomic arrangements to those in the analogous platinum compounds. The various reaction conditions for the Rb–Pd–H system are summarized in Fig. 9. Corresponding schemes to that in Fig. 9 could also be determined for the K–Pd–H and Cs–Pd–H systems [17]. The dependence upon pressure for the formation of particular ternary hydrides accords with the calculated volume increments for the hydride or deuteride ions in the alkali-metal hydrides and the ternary hydrides. Thus the volume decreases for the hydrogen atoms in the sequence $AH > A_3PdH_3 > A_2PdH_4 > A_3PdH_5$. The following volume increments were used for the calculations involving the hydrides listed in Fig. 9: Rb^+, 20 cm^3; Pd^0, 9 cm^3; Pd^{2+}, 4 cm^3 [18].

5. Alkali-metal rhodium and iridium hydrides

The first structurally-verified ternary alkali-metal hydrides of iridium and rhodium were Li_3IrH_6, Na_3IrH_6 and Na_3RhH_6 [3]. The determination of their crystal structures, carried out by means of a

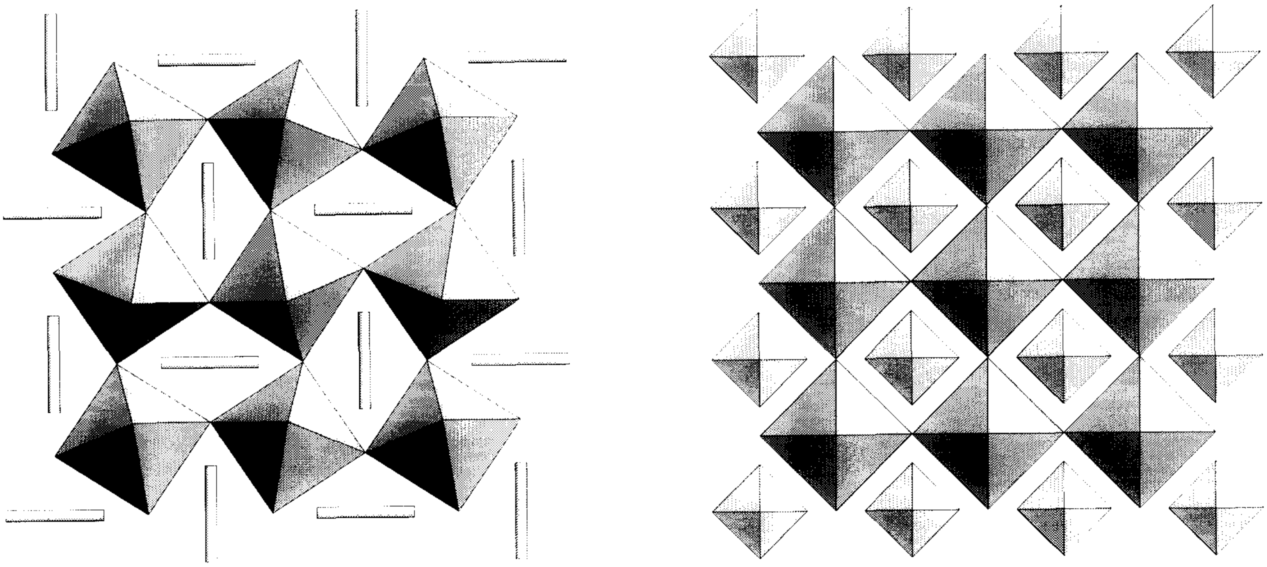

Fig. 8. Arrangement of the potassium octahedra and of the $[\mathrm{PdD}_2]^{2-}$ groups in (a) the tetragonal, low temperature modification of K_3PdD_3 and (b) its cubic, high temperature modification.

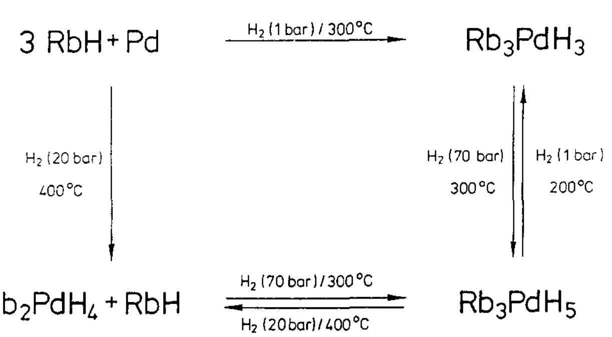

Fig. 9. Experimental conditions for the synthesis of the ternary hydrides in the system rubidium–palladium–hydrogen in a H_2-charged atmosphere.

combination of X-ray and neutron diffraction experiments on powdered samples, revealed the existence of complex $[\mathrm{MH}_z]^{x-}$ structural units: in this case almost regular $[\mathrm{IrH}_6]^{3-}$ and $[\mathrm{RhH}_6]^{3-}$ octahedra that are embedded in an alkali-metal matrix (Fig. 10).

In the Li–Rh–H system, the compound Li_3RhH_4 was obtained under similar synthesis conditions, i.e. 1 bar hydrogen pressure (Fig. 11) [19]. This contains square-planar $[\mathrm{RhH}_4]^{3-}$ groups which correlate with the d^8 electronic configuration of the central transition-metal ion. Following the observation that higher oxidation states of palladium can be stabilized in compounds when increased hydrogen pressures were utilized, the compound Li_3RhH_6 was subsequently prepared at 80 bar hydrogen pressure [20]. The determination of its structure showed, as expected, that it is isotypic with the above-mentioned hydrides Li_3IrH_6, Na_3IrH_6 and Na_3RhH_6.

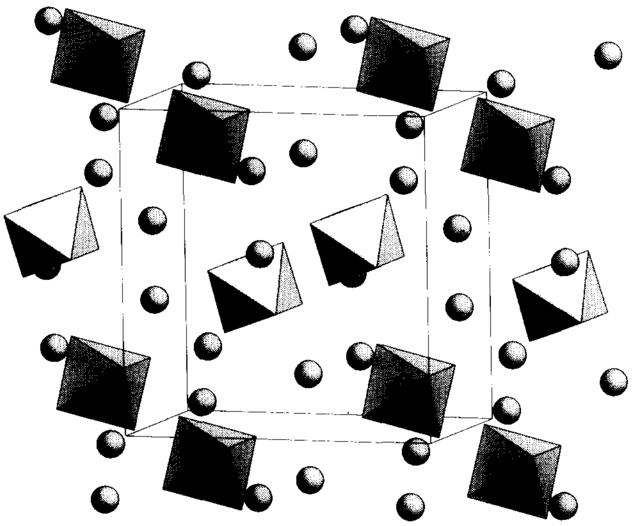

Fig. 10. Crystal structure of Na_3RhD_6, showing the $[\mathrm{RhD}_6]^{3-}$ octahedra and the positions of the sodium atoms.

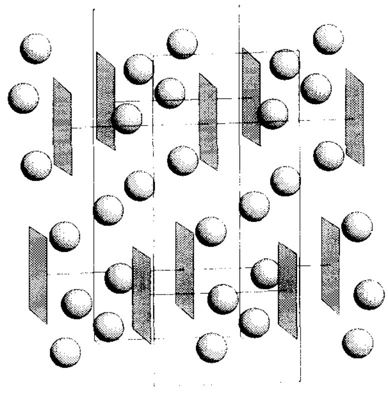

Fig. 11. Crystal structure of Li_3RhD_4, showing the planar $[\mathrm{RhD}_4]^{3-}$ groups and the positions of the lithium atoms.

Investigations into the existence of ternary hydrides of iridium and rhodium which contain the heavier alkali metals indicated that, although compounds in this area can be prepared, the determination of their crystal structures has, as yet, been unsuccessful.

6. Alkaline-earth transition-metal hydrides

In this area, several compounds containing the 4d metals of Group VIII have been synthesized and structurally characterized.

In the Ca–Pd–H system, the ternary hydride $CaPdH_2$ could be obtained which crystallizes with a perovskite-like atomic arrangement (Fig. 12) [21]. The hydrogen atoms fill the available sites with an occupancy factor of 2/3. Neutron diffraction experiments have revealed that no phase transition occurs down to 10 K, which indicates an ordered distribution of atoms. In this case there is probably no dynamic disorder of the hydrogen ligands but, instead, a statistical arrangement of linear $[PdH_2]^{2-}$ structural units over three dimensions without the formation of a superlattice. In the corresponding system containing strontium, the copper-red hydride $SrPdH_{2.7}$ has been prepared by the combination of an SrPd alloy with hydrogen in an exothermic reaction [22]. X-ray and neutron diffraction experiments also revealed a perovskite-type structure here in which the hydrogen atoms statistically fill the three-fold sites with an occupation factor of 0.91(4)

The hydride Sr_2RhH_5 has been known since 1971 [23]. A complete structural determination of the corresponding deuteride has yielded an atomic arrangement that corresponds with that in the K_2PtCl_6 type but with a statistical 5/6 occupation of the chlorine positions. A second strontium rhodium hydride, $Sr_8Rh_5H_{23}$ crystallizes with a structure that is a transition state between the K_2PtCl_6-type and the perovskite-type structures (see Fig. 13) [24].

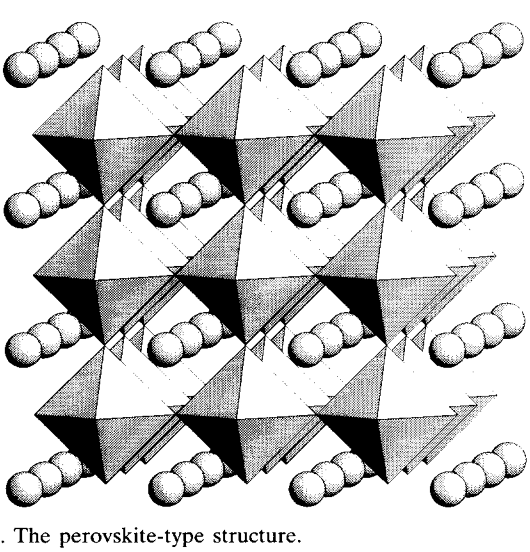

Fig. 12. The perovskite-type structure.

The compound Mg_2RuH_6 [25–27] also possesses an atomic arrangement corresponding to that in K_2PtCl_6. This hydride was simultaneously investigated in Stockholm, Genf and Aachen. Further compounds in this system which were characterized in conjunction with the research group in Genf are listed in Fig. 14. The synthesis conditions given are those used by the Aachen group in which all the reactions were carried out at a temperature of 780°C. Here again, the volume increment of the hydrogen atoms in resulting compounds decreases with increasing reaction pressure. The decrease in the sequence Mg_3RuD_6, Mg_2RuD_4, Mg_2RuD_6 is from 8.2 via 7.6 to 6.4 $cm^3\ mol^{-1}$. The orthorhombic structure of Mg_3RuH_6 is shown in Fig. 15 [28]. The atomic arrangement consists of two types of hydrogen atoms which are differently bonded; one coordinates the ruthenium atoms with a statistical, deficient occupation of the octahedral sites, whereas the other is exclusively coordinated by magnesium atoms. The characteristic structural units of Mg_2RuH_4 are $[RuH_4]^{4-}$ anions that derive from the octahedral configuration of the $[RuH_6]^{4-}$ groups via the omission of two cis-ligands [29]. This hitherto unknown coordination geometry for a transition-metal ion with a d^8 electron configuration is evidently stabilized by the existence of metal–metal interactions between the ruthenium atoms in the direction of the missing cis-ligands (see Fig. 16). The Ru–Ru atomic distance in this compound is 3.236(4) Å.

The above-mentioned metal–metal interactions are noteworthy but not unique since they occur not only in the structure of Mg_2RuH_4 but also in the previously-described hydrides Li_3RhH_4 [19] and Na_2PdH_2 [10] (see Figs. 6 and 11). Initial investigations into their physical properties showed that these compounds are transition states between the more salt-like hydrides and the more covalent-metallic hydrides. Thus, Na_2PdH_2 has been revealed to act as a semiconductor [30]. This transition has not been observed with the analogously-composed ternary halogenides. Hydrogen is indeed an unusual ligand.

7. Synthesis of metal hydrides at high hydrogen pressures with a view towards synthesis schemes

In the area of the ternary hydrides of palladium, rhodium and ruthenium, various compounds can be synthesized dependent upon the hydrogen reaction pressure. The above-mentioned examples show that higher oxidation states of the transition metals can be

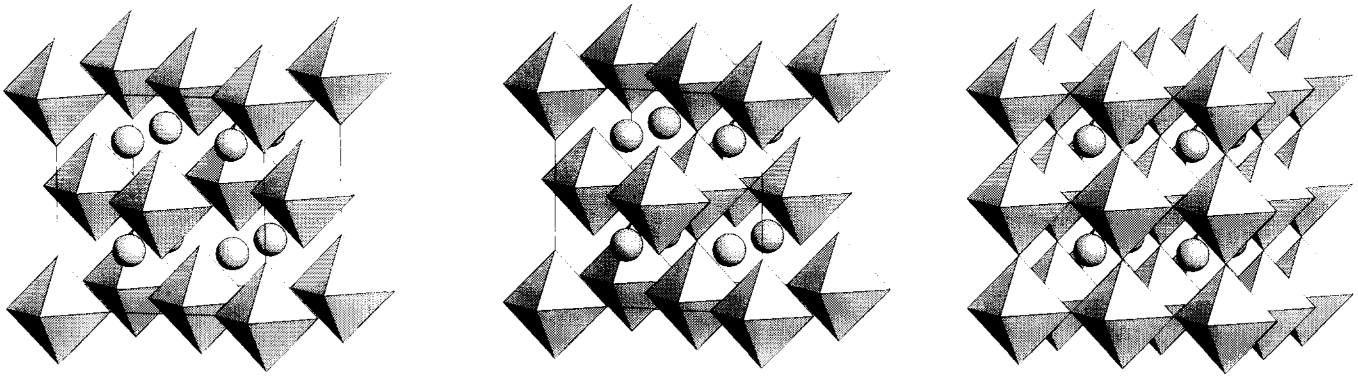

Fig. 13. (a) The K_2PtCl_6-type structure; (b) the $Sr_8Rh_5H_{23}$-type structure; (c) the perovskite-type structure.

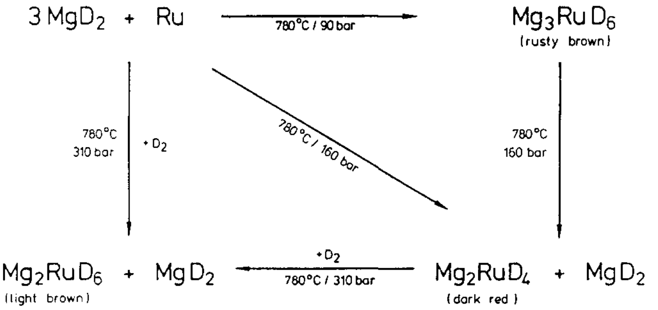

Fig. 14. Experimental conditions for the synthesis of the ternary deuterides in the system magnesium-ruthenium-deuterium in a D_2-charged atmosphere.

stabilized with increasing hydrogen pressure; i.e. the oxidative power of hydrogen increases with increasing pressure. Nevertheless, it was evidently not sufficient to attain the highest oxidation states, as present, for example, in the corresponding chlorides and fluorides. Recently we have succeeded in reaching hydrogen reaction pressures of up to 3000 bar at a temperature of 700°C using our self-built high pressure autoclaves (see Fig. 17). Under corresponding conditions we have succeeded in synthesizing the ternary palladium(II) hydride Na_2PdH_4 [31] such that the palladium is oxidized beyond oxidation state zero. Neutron diffraction experiments yielded a complete structure determination in which the atomic arrangement is isotypic to that in Na_2PtH_4. However, the real breakthrough occurred with the ternary platinum compounds. Under higher hydrogen pressures we were able to prepare Na_2PtH_6 [32], K_2PtH_6 [33], Rb_2PtH_6 [34] and Cs_2PtH_6 [34], i.e. hydrogen has oxidized the platinum from oxidation state zero to oxidation state +4. All four compounds crystallize with the K_2PtCl_6-type structure.

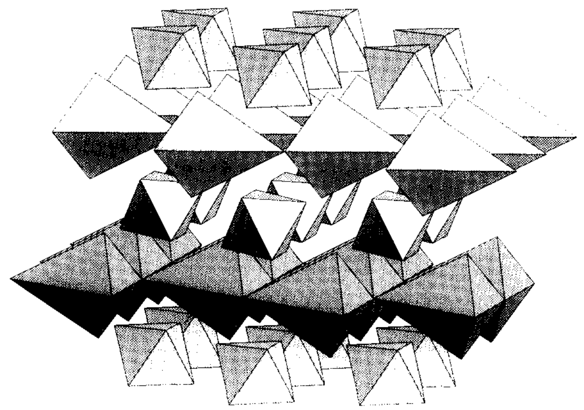

Fig. 15. Atomic arrangement of Mg_3RuD_6, showing the vertex-shared magnesium trigonal-bipyramids, which have hydride ions at their centres and the ruthenium-deuterium octahedra with an occupancy factor of 3/4.

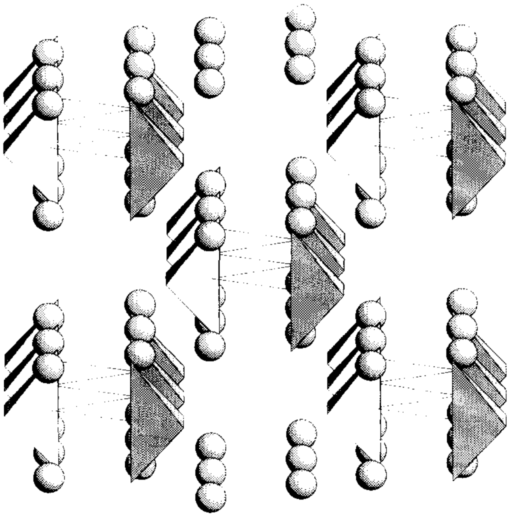

Fig. 16. Atomic arrangement of Mg_2RuD_4, showing the positions of the magnesium atoms and the $[RuD_4]^{4-}$ groups that derive from the octahedral configuration of the $[RuD_6]^{4-}$ groups via the omission of two cis-ligands. The lines show the Ru-Ru interactions.

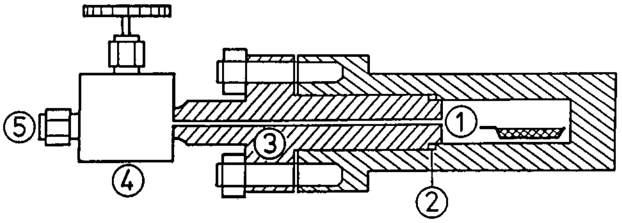

Fig. 17. High pressure autoclave: (1) reaction boat; (2) copper gasket; (3) inner ram cylinder; (4) high pressure valve; (5) connection for hydrogen–vacuum–pressure gauge.

It is reasonable to suppose that further, hitherto unknown metal hydrides can be prepared using these high pressure syntheses, possibly also containing transition metals that lie further to the left in the periodic table from Group VIII.

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References

[1] W. Bronger, P. Müller, D. Schmitz and H. Spittank, *Z. Anorg. Allg. Chem.*, *516* (1984) 35.
[2] W. Bronger, *Angew. Chem. Int. Ed. Engl.*, *30* (1991) 759.
[3] W. Bronger, M. Gehlen and G. Auffermann, *J. Alloys Comp.*, *176* (1991) 255.
[4] B. Nacken and W. Bronger, *Z. Anorg. Allg. Chem.*, *439* (1978) 29.
[5] W. Bronger, G. Auffermann and P. Müller, *J. Less-Common Met.*, *116* (1986) 9.
[6] W. Bronger, G. Auffermann and P. Müller, *J. Less-Common Met.*, *142* (1988) 243.
[7] W. Bronger, R.P. Jung and G. Neue, *Acta Crystallogr. A*, *46* (1990) C366.
[8] W. Bronger, G. Auffermann and P. Müller, *Z. Anorg. Allg. Chem.*, *566* (1988) 31.
[9] B.G. Müller, *Z. Anorg. Allg. Chem.*, *491* (1982) 245.
[10] D. Noréus, K.W. Törnroos, A. Börje, T. Szabó, W. Bronger, H. Spittank, G. Auffermann and P. Müller, *J. Less-Common Met.*, *139* (1988) 233.
[11] R. Hoppe and H.-J. Röhrborn, *Z. Anorg. Allg. Chem.*, *329* (1964) 110.
[12] K. Kadir and D. Noréus, *Z. Phys. Chem. N.F.*, *163* (1989) 231.
[13] B. Nacken and W. Bronger, *J. Less-Common Met.*, *52* (1977) 323.
[14] W. Bronger and G. Auffermann, *J. Less-Common Met.*, *158* (1990) 163.
[15] K. Kadir, M. Kritikos, D. Noréus and A.F. Andresen, *J. Less-Common Met.*, *172* (1991) 36.
[16] W. Bronger and G. Auffermann, *J. Alloys Comp.*, *187* (1992) 87.
[17] W. Bronger and G. Auffermann, *J. Alloys Comp.*, *187* (1992) 81.
[18] W. Biltz, *Raumchemie der festen Stoffe*, Verlag von Leopold Voss, Leipzig, 1934.
[19] W. Bronger, P. Müller, J. Kowalczyk and G. Auffermann, *J. Alloys Comp.*, *176* (1991) 263.
[20] W. Bronger, M. Gehlen and G. Auffermann, *Z. Anorg. Allg. Chem.*, *620* (1994) 1983.
[21] W. Bronger, K. Jansen, P. Müller, *J. Less-Common Met.*, *161* (1990) 299.
[22] W. Bronger and G. Ridder, *J. Alloys Comp.*, *210* (1994) 53.
[23] R.O. Moyer, C. Stanitski, J. Tanaka, M.I. Kay and R. Kleinberg, *J. Solid State Chem.*, *3* (1971) 541.
[24] W. Bronger, R. Beißmann and G. Ridder, *J. Alloys Comp.*, *203* (1994) 91.
[25] K. Jansen, *Thesis*, RTWH Aachen, 1990.
[26] B. Huang, F. Bonhomme, P. Selvam, K. Yvon and P. Fischer, *J. Less-Common Met.*, *171* (1991) 301.
[27] M. Kritikos and D. Noréus, *J. Solid State Chem.*, *93* (1991) 256.
[28] W. Bronger, K. Jansen and G. Auffermann, *J. Alloys Comp.*, *199* (1993) 47.
[29] F. Bonhomme, K. Yvon, G. Triscone, K. Jansen, G. Auffermann, P. Müller, W. Bronger and P. Fischer, *J. Alloys Comp.*, *178* (1992) 161.
[30] W. Bronger, in B. Krebs (ed.), *Unkonventionelle Wechselwirkungen in der Chemie metallischer Elemente*, VCH, Weinheim, 1992.
[31] W. Bronger and G. Auffermann, *J. Alloys Comp.*, *228* (1995) 119.
[32] W. Bronger and G. Auffermann, *J. Alloys Comp.*, *219* (1995) 45.
[33] W. Bronger and G. Auffermann, *Angew. Chem. Int. Ed. Engl.*, *33* (1994) 1112.
[34] W. Bronger and G. Auffermann, *J. Anorg. Allg. Chem.*, *621* (1995), in press.