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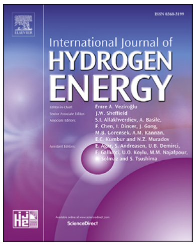

NH_3BH_3 as an internal hydrogen source for high pressure experiments

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ABSTRACT

Aminoborane NH_3BH_3 is proposed as an appropriate material to produce hydrogen in the high-pressure cells designed for the synthesis of hydrides in sizeable amounts at pressures of a few GPa and elevated temperatures. Aminoborane is a non-hydroscopic material and it does not noticeably react with air that permits assembling the high-pressure cells under ambient conditions without any precautions. If heated to 300 °C at any pressure from 0.6 to 9 GPa, aminoborane decomposes to H_2 gas and chemically inert amorphous BN and does not further absorb the liberated hydrogen. Experiments using NH_3BH_3 and AlH_3 alternatively as the internal hydrogen source gave coinciding isotherms of hydrogen solubility in rhodium at 600 °C and pressures up to 9 GPa therefore demonstrating that the partial pressure of impurities (if any) in the H_2 gas generated by NH_3BH_3 is well below the accuracy ±0.3 GPa of determination of the total gas pressure.

Introduction

Most hydrides discovered recently (e.g., PtH [1], RhH_2 [2], IrH_3 [3], FeH_2 and FeH_3 [4], RuH [5]) have been synthesized at high hydrogen pressures and room temperature using diamond anvil cells. The reaction volume of these apparatus is filled with molecular hydrogen prior to the experiment that warrants the hydrogen purity. In view of the small size of the samples (of the order of 0.01 mm^3 or even less), most new high-pressure hydrides were only studied by *in situ* X-ray diffraction, which determined the structures of their metal lattices. To explore other properties of high-pressure hydrides, more and more methods of *in situ* measurements in diamond anvils are being developed by different research groups, such as the methods of measuring the electrical resistance [6], X-ray absorption and X-ray magnetic circular dichroism (XMCD) [7], Mössbauer [8,9] and optical [10,11] spectra and many others.

At the same time, the determination of some important properties of the high-pressure hydrides (e.g., measuring their hydrogen content by a direct method like thermal desorption, or establishing the full crystal and magnetic structures by neutron diffraction, or studying the lattice dynamics by inelastic neutron scattering, etc.) still requires much larger samples. At pressures up to a few GPa and temperatures up to a few hundred degrees Celsius, hydride samples amounting to dozens mm^3 can be synthesized using multi-anvil apparatus (mostly employed by research groups in Japan [12–14]) or Toroid-type apparatus (used by our group [15,16]). In these apparatus made of hard alloys, hydrogen is produced *in situ*, from the material placed in the high-pressure cell together with the sample (see Figs. 1 and 2) and decomposed by heating

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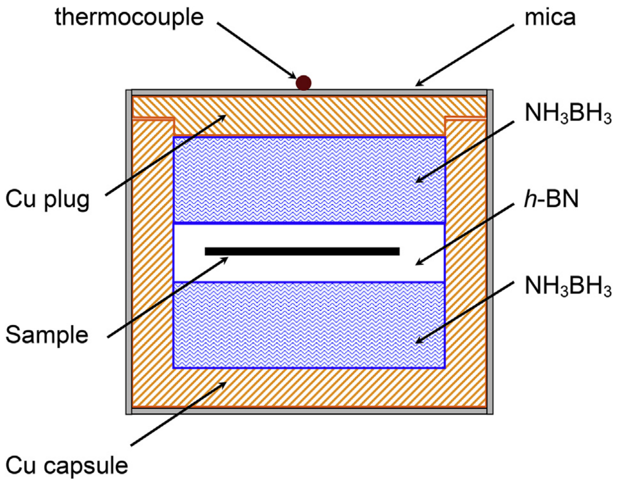

Fig. 1 – Schematic diagram of a high-pressure cell with aminoborane NH_3BH_3 used as a solid hydrogen source [16]. The external diameter of the cell is 8.5 mm, the thickness of its walls varies from 0.7 mm in the experiments at 400 °C to 1.5 mm at 800 °C.

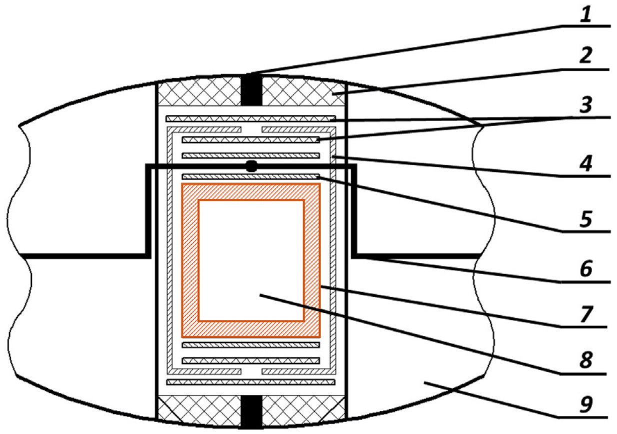

Fig. 2 – Schematic diagram of the high-pressure assembly with a Nichrome heater. 1 – current lead to the heater (Nichrome); 2 – electric and thermal insulator (limestone); 3 – thin electric and thermal conductive discs (copper); 4 – squirrel-type heater (Nichrome); 5 – spacer (limestone); 6 – thermocouple (Chromel–Alumel); 7 – high-pressure cell (copper) wrapped in mica; 8 – working zone; 9 – gasket (limestone) of the Toroid-type high-pressure apparatus.

at a pressure of 1–3 GPa or higher, when the liberated hydrogen is already dense. The cell is made of the material largely impermeable to hydrogen (Teflon [15], Cu [15,16], NaCl [12–14], etc.); the sample is protected from direct contact with the hydrogen source by a layer of kaolin wool [15] or hexagonal BN (e.g., [13,16]).

To produce hydrogen inside the cell, our group mostly uses AlH_3 proposed for this purpose in Ref. [17]. Thermal decomposition of chemically prepared AlH_3 produces only Al and pure H_2. Using AlH_3 and Toroid-type apparatus allowed us, in particular, to synthesize hydrides of Fe, Co, Mo, Rh and Re [15].

The most impressive result of using AlD_3 in a multi-anvil apparatus is the recent *in situ* determination of the full crystal structure of *fcc* (face centered cubic) iron deuteride at 6.3 GPa and 715 °C by neutron diffraction [14].

The usage of AlH_3 as the internal hydrogen source in the high-pressure cells has, however, certain limitations. The Al particles resulting from the decomposition of AlH_3 at temperatures above the upper curve (violet one in the web version) in Fig. 3 [18] can further absorb the released hydrogen and form AlH_3 if exposed to *P*, *T* conditions below the equilibrium line of the $Al + (3/2)H_2 = AlH_3$ reaction shown in Fig. 3 by the lower curve (red one in the web version) [19]. The amount of the absorbed hydrogen becomes significant at $P > 5$ GPa. At a pressure of 9 GPa, it can reach from 0.3 to 0.8 of the initial hydrogen release. Besides, the Al particles are chemically active and should carefully be isolated from the sample and from the walls of the high-pressure cell, if it is made of a metal.

In the multi-anvil apparatus of the Japanese high-pressure groups, hydrogen is usually produced by thermal decomposition of alumohydrides or by thermally activated reaction between borohydrides and $Ca(OH)_2$. Regretfully, the by-products (yet unidentified) of the hydrogen release in these processes seem to be too chemically active. Particularly, the *fcc* high-pressure high-temperature phases of manganese synthesized using $LiAlH_4$ as the hydrogen source [20] had the atomic volume and magnetic properties unrealizable for the *fcc* manganese hydrides [21]; the *fcc* high-pressure high-temperature phase of molybdenum obtained in the experiments with hydrogen produced by a reaction between $NaBH_4$ and $Ca(OH)_2$ [13] was not a binary Mo–H hydride either [16].

The present paper proposes NH_3BH_3 as a more convenient material to produce hydrogen in the high-pressure cells

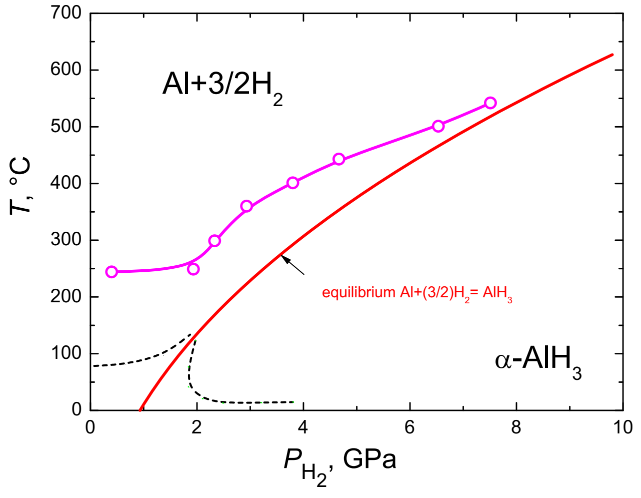

Fig. 3 – Experimental baric dependence of the decomposition temperature of chemically prepared AlH_3 powder stabilized by a surface oxide layer [18] (open magenta circles) and the equilibrium line of the $Al + (3/2) H_2 = AlH_3$ reaction [19] (solid red curve; the dashed black curves show the reaction hysteresis rapidly growing at temperatures below 150 °C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

designed for high-temperature experiments. Such a recommendation might look questionable because the thermal decomposition (pyrolysis) of NH_3BH_3 at low pressures is known to be a complex, multi-stage process including formation of volatile intermediate compounds. However, according to Ref. [22], the only products of this process surviving at $T > 200$ °C are solid BN and H_2 gas.

Encouraged by the latter result, we examined at $T \leq 800$ °C and $P \leq 6$ GPa the reaction of molybdenum with the gas obtained by decomposition of aminoborane after its relatively rapid heating (within a few minutes) to 300 °C at a pressure of 1.5 GPa [16]. Experiment showed no contamination of the hydrogenated metal with nitrogen or boron.

In the present paper, we constructed isotherms of hydrogen solubility in rhodium metal at $T = 600$ °C and $P \leq 9$ GPa using NH_3BH_3 and alternatively AlH_3 as the internal hydrogen source. Rhodium is known to form a hydride via an isomorphic phase transition at hydrogen pressures of 4–5 GPa [23] and our idea was to examine if the transition pressure was independent on the hydrogen source, NH_3BH_3 or AlH_3. The isotherms of hydrogen solubility were constructed using a quenching technique. After the hydrogenation of the sample at 600 °C and pre-selected pressure was complete, it was rapidly cooled (quenched) to the liquid N_2 temperature to prevent further changes in the hydrogen content. The phase composition of the quenched samples was further examined by X-ray diffraction at ambient pressure and their hydrogen content was determined by thermal desorption.

Experimental details

The 99% pure NH_3BH_3 used in the present work was prepared by the method of [24] and further recrystallized from a solution in dehydrated alcohol. The 99.2% pure AlH_3 was synthesized as described by Brower et al. [25]. The starting rhodium samples were in the form of $3.5 \times 3.5 \times 0.1$ mm^3 platelets cut out of a polycrystalline foil of 99.99% Rh metal.

The rhodium platelets were hydrogenated in the high-pressure cells schematically shown in Fig. 1. The cells were nearly identical to those used to hydrogenate molybdenum in our recent paper [16] and similar to the cells proposed by Wakamori et al. [17] for the synthesis of rare-earth hydrides many years ago. In our experiments at 600 °C, the cells had an outer diameter of 8.5 mm and a wall thickness of 1 mm. When AlH_3 was used as the internal hydrogen source, it was additionally isolated from the walls of the copper cell by a layer of mica in order to prevent their reaction with Al particles formed after the decomposition of the hydride.

The assembled cell was compressed in a quasihydrostatic Toroid-type high-pressure apparatus [26] with a squirrel-type heater made of Nichrome wire 0.5 mm in diameter (Fig. 2). A 0.2 mm layer of mica electrically isolated the cell from the heater and from the thermocouple used to determine the temperature of the sample with an accuracy of ±15 °C. To prevent the limestone of the gasket from transformation to the denser aragonite-type modification at elevated temperatures, it was separated from the heater by a pyrophyllite sleeve (not shown in Fig. 2) with an outer diameter of 13 mm. The sleeve was preliminarily dehydrated in air at 650 C for 30 min. The pressure in the cell was estimated with an accuracy of ±0.3 GPa using the relationship between the pressure and ram load determined in separate room-temperature experiments.

In each experiment, the high-pressure cell was first compressed to ~1.5 GPa at room temperature, heated during a few minutes to 300 °C and kept under these conditions for 10 min in order to decompose the NH_3BH_3 or AlH_3 compound served as the internal hydrogen source. The samples were hydrogenated by a 30 min exposure to the resulting H_2 atmosphere at a temperature of 600 °C and pre-selected pressure followed by rapid cooling (quenching) together with the Toroid-type apparatus to room temperature in 15 s and further to ~80 K in 20 min. The pressure was then released; the apparatus was disassembled under liquid nitrogen; the sample was retrieved from the cell and stored in liquid N_2 until the measurements.

Each hydrogenated sample was examined by X-ray diffraction at 85 K with a Siemens D500 diffractometer using Cu Kα radiation selected by a diffracted beam monochromator. The diffractometer was equipped with a home-designed nitrogen cryostat that permitted the samples to be loaded without any intermediate warming. The obtained diffraction patterns were analyzed using POWDERCELL2.4 software.

The hydrogen content of the samples was determined with a relative accuracy of 3% by thermodesorption of hydrogen into a pre-evacuated measuring system in the regime of heating from 85 K to 440 °C at a rate of 10 °C/min. The mass of the analyzed probe was a few milligrams. The method is described in more detail elsewhere [27].

Results and discussion

Our preliminary experiments showed that the hydrogen content of the Rh–H samples stopped changing after a 10 min exposure to the synthesis conditions. On the other hand, in spite of the high hydrogen diffusivity at 600 °C, the 1 mm thickness of the copper walls of the high-pressure cell warranted the retention of a hydrogen atmosphere around the sample for a few hours at pressures up to 6 GPa and for not less than 1 h at 9 GPa. The chosen hydrogenation time of 30 min was therefore sufficient for the samples to reach the stationary hydrogen compositions in contact with the H_2 gas taken in excess.

The $\gamma_1 \leftrightarrow \gamma_2$ transformation between the dilute (γ_1 phase) and concentrated (γ_2 hydride) solid hydrogen solutions in *fcc* Rh was earlier studied at temperatures up to 400 °C by measuring the electrical resistance of the samples [23]. Within the experimental error of ±0.5 GPa, the equilibrium pressure of the $\gamma_1 \leftrightarrow \gamma_2$ transformation did not depend on temperature and lied between 4 and 5 GPa at $50 \leq T \leq 400$ °C, and the baric hysteresis of the transformation vanished at $T > 250$ °C. One could therefore expect that at a temperature of 600 °C chosen for the investigation in the present work, the $\gamma_1 \leftrightarrow \gamma_2$ transformation would occur at a similar pressure and show very small baric hysteresis.

As seen from Fig. 4, the $\gamma_1 \leftrightarrow \gamma_2$ transformation in the Rh–H system did occur in the expected pressure interval and was accompanied with a step-wise increase of the hydrogen

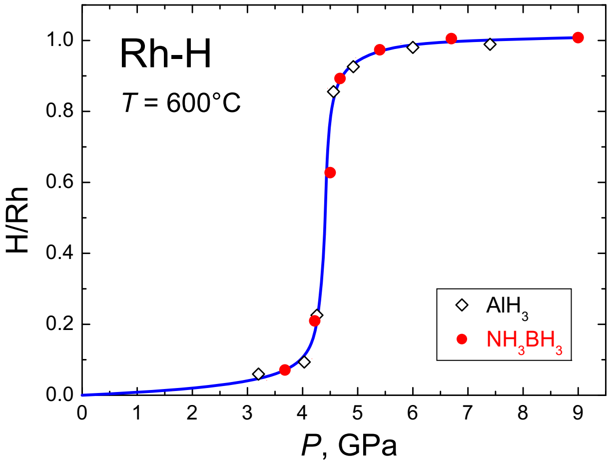

Fig. 4 – Isotherm of the hydrogen solubility in rhodium at 600 °C. The Rh–H samples were synthesized in the high-pressure cells shown in Fig. 1 using AlH_3 (open diamonds) or NH_3BH_3 (filled circles) as the internal source of hydrogen. The hydrogen content was determined by thermal desorption of the gas from quenched Rh–H samples.

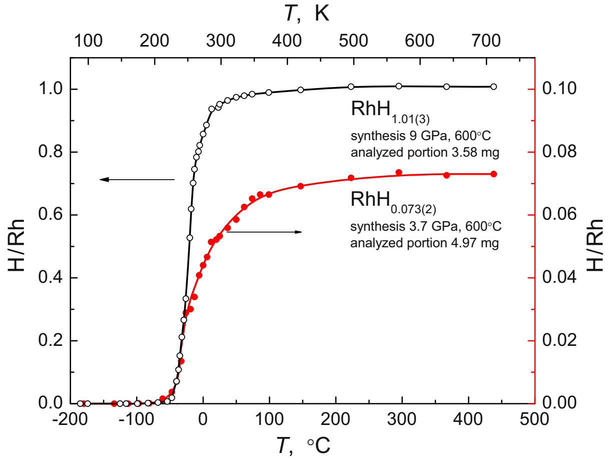

Fig. 5 – Temperature dependences of the amount of hydrogen released from the quenched Rh–H samples heated at 10 °C/min in a closed-volume, pre-evacuated measuring system.

solubility from a few atomic per cent in the in γ_1 phase to an atomic ratio H/Rh of $x \approx 1$ in the γ_2 hydride. The x(P) dependences for the samples synthesized using AlH_3 and NH_3BH_3 as the internal hydrogen source nearly coincided and could be represented by a common curve with a step midpoint at $P = 4.4(3)$ GPa. This is the principle result of the present paper. Considering that AlH_3 generates high purity hydrogen [19], the coinciding transition pressures would demonstrate that the hydrogen gas produced by NH_3BH_3 is pure enough to reliably construct phase diagrams of the metal-hydrogen systems in the GPa pressure range at temperatures of up to 600 °C, at least.

Some new results concerning the Rh–H system may also be of interest. While the hydrogen content $x \approx 1$ and the lattice parameter $a = 4.021(2)$ Å of the single-phase γ_2 samples synthesized at 600 °C were the same as those of the γ_2 samples obtained at $T \leq 400$ °C [23], no hydrogen solubility was earlier detected in the γ_1 phase. Our X-ray diffraction study of the quenched Rh–H samples with $x \leq 0.1$ prepared at 600 °C and pressures up to 4 GPa (below the pressure of the $\gamma_1 \rightarrow \gamma_2$ transition, see Fig. 4) showed them to be mostly composed of the γ_1 phase with the lattice parameter $a = 3.804(2)$ Å noticeably exceeding $a = 3.792(2)$ Å of the initial Rh foil at the measuring temperature of 85 K. The increased value of the lattice parameter could not, however, be directly related with the mean hydrogen content of samples, because they contained a certain amount of the γ_2 phase, too, traces of which were seen in the X-ray patterns. A considerable contribution from the γ_2 phase to the total hydrogen content of the Rh–H sample prepared at 3.7 GPa can also be inferred from the presence of a large step on its decomposition curve in the temperature interval from −50 to −20 °C of the intensive hydrogen release from the γ_2 sample synthesized at 9 GPa (Fig. 5). The hydrogen content of the γ_1 phase retained in the quenched Rh–H samples can roughly be estimated as $x \sim 0.05$ from the value of its lattice parameter assuming a linear concentration dependence a(x) of solid hydrogen solutions in *fcc* Rh in the full concentration range from $x = 0$ to $x = 1$.

A few years ago [2], rhodium was discovered to form a dihydride at room temperature and a hydrogen pressure of 8 GPa, and this new phase proved to be thermally stable at ambient pressure and $T = 77$ K and started rapidly decomposing only after heating to 150 K. The experiments were carried out on a powder Rh sample in a diamond anvil cell by X-ray diffraction using synchrotron radiation. Our efforts to prepare a bulk sample of RhH_2 at a hydrogen pressure of 9 GPa and temperatures from 25 to 600 °C, however, failed. Most likely, the formation pressure of RhH_2 is higher than 9 GPa in the case of bulk samples because of the larger baric hysteresis caused by the elastic stresses. The formation of RhH_2 at room temperature and a hydrogen pressure of 10.5 GPa has recently been confirmed by X-ray diffraction experiments in a diamond anvil cell using a Rh foil with a “macroscopic” thickness of 10 μm [28].

We also used the experiments with Rh at a pressure of 9 GPa to learn more about the thermal stability of NH_3BH_3 at high pressures. Particularly, we compared products of two different experiments of a 24 h hydrogenation of Rh at 9 GPa and 300 °C followed by quenching the high-pressure cell to the liquid nitrogen temperature. In one experiment, the hydrogen was produced inside the cell via our standard procedure of decomposing NH_3BH_3 by heating to 300 °C at 1.5 GPa. In another experiment, the cell was first compressed to 9 GPa at room temperature and then heated to 300 °C. The two experiments gave identical results. The Rh metal transformed to the γ_2 hydride with $x \approx 1$, while NH_3BH_3 decomposed to hydrogen and amorphous boron nitride with an X-ray diffraction pattern similar to that presented in Fig. 7 of Ref. [29]. The transformation of NH_3BH_3 to amorphous BN was also observed in all our experiments at other pressures and the BN thus produced always contained hydrogen at the level of a molar ratio of $H_2/BN \approx 0.08$–0.1. This relatively small amount of residual hydrogen (compared to $H_2/BN = 3$ of the starting NH_3BH_3 compound) was likely to be adsorbed on the surface of BN particles and it left the quenched material on heating in vacuum to 20–80 °C.

The decomposition of NH_3BH_3 at a pressure of 9 GPa demonstrates that the compound remains thermodynamically unstable up to this pressure. Such instability is an important advantage of NH_3BH_3 compared to AlH_3, which easily releases hydrogen in heating above 250 °C at pressures up to about 2 GPa, but begins to absorb it back in considerable amounts at pressures above 5 GPa and moderate temperatures of 250–600 °C below the equilibrium line of the $Al + (3/2) H_2 = AlH_3$ reaction [19] shown in Fig. 3 by the lower curve (red one in the web version).

Conclusions

Aminoborane NH_3BH_3 is shown to be a good material for the use as internal hydrogen source in large-volume high-pressure apparatus working at elevated temperatures in the GPa pressure range. Compared to AlH_3 proposed for this purpose many years ago [17] and later successfully used to synthesize and study a number of new high-pressure hydrides (see, e.g., [15] and [14]), aminoborane has the following advantages: *i*) NH_3BH_3 irreversibly decomposes to H_2 and BN when heated to 300 °C at pressures up to 9 GPa and does not absorb the released hydrogen at $P \leq 9$ GPa and $T \leq 600$ °C; *ii*) the residual BN is one of the most chemically inert materials in contrast to the very active Al metal resulting from decomposition of AlH_3. Despite the complex reaction path of thermal decomposition of aminoborane, the partial pressure of impurities in the H_2 gas produced by heating NH_3BH_3 above 300 °C in the GPa pressure range is vanishingly small that allows an accurate investigation of phase diagrams of metal-hydrogen systems.

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REFERENCES

[1] Scheler T, Degtyareva O, Marqués M, Guillaume CL, Proctor JE, Evans S, et al. Synthesis and properties of platinum hydride. Phys Rev B 2011;83:214106. http://dx.doi.org/10.1103/PhysRevB.83.214106.

[2] Li B, Ding Y, Kim DY, Ahuja R, Zou G, Mao H-K. Rhodium dihydride (RhH_2) with high volumetric hydrogen density. PNAS 2011;108:18618–21. http://dx.doi.org/10.1073/pnas.1114680108.

[3] Scheler T, Marqués M, Konôpková Z, Guillaume CL, Howie RT, Gregoryanz E. High-pressure synthesis and characterization of iridium trihydride. Phys Rev Lett 2013;111:215503. http://dx.doi.org/10.1103/PhysRevLett.111.215503.

[4] Pépin CM, Dewaele A, Geneste G, Loubeyre P, Mezouar M. New iron hydrides under high pressure. Phys Rev Lett 2014;113:265504. http://dx.doi.org/10.1103/PhysRevLett.113.265504.

[5] Kuzovnikov MA, Tkacz M. Synthesis of ruthenium hydride. Phys Rev B 2016;93:064103. http://dx.doi.org/10.1103/PhysRevB.93.064103.

[6] Matsuoka T, Hirao N, Ohishi Y, Shimizu K, Machida A, Aoki K. Structural and electrical transport properties of FeH_x under high pressures and low temperatures. High Press Res 2011;31(1):64–7. http://dx.doi.org/10.1080/08957959.2010.522447.

[7] Ishimatsu N, Shichijo T, Matsushima Y, Maruyama H, Matsuura Y, Tsumuraya T, et al. Hydrogen-induced modification of the electronic structure and magnetic states in Fe, Co, and Ni monohydrides. Phys Rev B 2012;86:104430. http://dx.doi.org/10.1103/PhysRevB.86.104430.

[8] Matsuoka T, Fujihisa H, Hirao N, Ohishi Y, Mitsui T, Masuda R, Seto M, Yoda Y, Shimizu K, Machida A, Aoki K. Structural and valence changes of europium hydride induced by application of high-pressure H_2. Phys Rev Lett 2011;107:025501. http://dx.doi.org/10.1103/PhysRevLett.107.025501.

[9] Mitsui T, Masuda R, Seto M, Hirao N, Matsuoka T, Nakamura Y, et al. In situ synchrotron ^{57}Fe Mössbauer spectroscopy of RFe_2 (R = Y, Gd) hydrides synthesized under ultra-high-pressure hydrogen. J Alloys Compd 2013;580:S264–7. http://dx.doi.org/10.1016/j.jallcom.2013.03.271.

[10] Wijngaarden RJ, Huiberts JN, Nagengast D, Rector JH, Griessen R, Hanfland M, et al. Towards a metallic YH_3 phase at high pressure. J Alloys Compd 2000;308:44–8. http://dx.doi.org/10.1016/S0925-8388(00)00913-0.

[11] Kume T, Ohura H, Sasaki S, Shimizu H, Ohmura A, Machida A, et al. High-pressure study of YH_3 by Raman and visible absorption spectroscopy. Phys Rev B 2007;76:024107. http://dx.doi.org/10.1103/PhysRevB.76.024107.

[12] Fukai Y. The metal-hydrogen system. Berlin: Springer; 2005.

[13] Fukai Y, Mizutani M. The phase diagram of Mo–H alloys under high hydrogen pressures. Mater Trans 2003;44(7):1359–62. http://dx.doi.org/10.2320/matertrans.44.1359.

[14] Machida A, Saitoh H, Sugimoto H, Hattori T, Sano-Furukawa A, Endo N, et al. Site occupancy of interstitial deuterium atoms in face-centred cubic iron. Nat Commun 2014;5:5063. http://dx.doi.org/10.1038/ncomms6063.

[15] Antonov VE. Phase transformations, crystal and magnetic structures of high-pressure hydrides of d-metals. J Alloys Compd 2002;330–332:110–6. http://dx.doi.org/10.1016/S0925-8388(01)01532-8.

[16] Abramov SN, Antonov VE, Bulychev BM, Fedotov VK, Kulakov VI, Matveev DV, et al. *T-P* phase diagram of the Mo-H system revisited. J Alloys Compd 2016;672:623–9. http://dx.doi.org/10.1016/j.jallcom.2016.02.209.

[17] Wakamori K, Filipek SM, Sawaoka A. Convenient method for the synthesis of rare-earth hydrides by the use of a conventional very high pressure technique. Rev Sci Instrum 1983;54:1410–1. http://dx.doi.org/10.1063/1.1137257.

[18] Belash IT. Stability of some intermediate compounds under high pressure. Doctoral Thesis. Chernogolovka: Institute of Solid State Physics; 1976 (in Russian).

[19] Graets J, Reilly JJ, Yartys VA, Maehlen JP, Bulychev BM, Antonov VE, et al. J Alloys Compd 2011;509S:S517–28. http://dx.doi.org/10.1016/j.jallcom.2010.11.115.

[20] Fukai Y, Ishikawa H, Goto T, Susaki J, Yagi T, Soubeyroux JL, et al. High-pressure synthesis and magnetic properties of cubic manganese hydride. Z Phys Chem N F 1989;163:479–82. http://dx.doi.org/10.1524/zpch.1989.163.Part_2.0479.

[21] Fedotov VK, Antonov VE, Kolesnikov AI, Beskrovnyi AI, Grosse G, Wagner FE. Neutron diffraction investigation of γ manganese hydride. Solid State Commun 1998;107:787–90. http://dx.doi.org/10.1016/S0038-1098(98)00229-4.

[22] Storozhenko PA, Svitsyn RA, Ketsko VA, Buryak AK, Ul'yanov AV. Ammineborane: synthesis and physicochemical

characterization. Zh Neorgan Khim 2005;50(7):1066–71 [Engl. Trans. Russian J Inorg Chem. 2005;50(7):980–985].

[23] Antonov VE, Belash IT, Malyshev VY, Ponyatovsky EG. The solubility of hydrogen in the platinum metals under high pressure (Reprinted from Platinum Metals Review, vol. 28, 1984). Int J Hydrogen Energy 1986;11(3):193–7. http://dx.doi.org/10.1016/0360-3199(86)90083-2.

[24] Shore SG, Parry RW. Chemical evidence for the structure of the "Diammoniate of Diborane." II. The preparation of ammonia-borane. J Am Chem Soc 1958;80(1):8–12. http://dx.doi.org/10.1021/ja01534a003.

[25] Brower FM, Matzek NE, Reigler PF, Rinn HW, Roberts CB, Schmidt DL, et al. Preparation and properties of aluminum hydride. J Am Chem Soc 1976;98(9):2450–3. http://dx.doi.org/10.1021/ja00425a011.

[26] Khvostantsev LG, Slesarev VN, Brazhkin VV. Toroid type high-pressure device: history and prospects. High Press Res 2004;24(3):371–83. http://dx.doi.org/10.1080/08957950412331298761.

[27] Bashkin IO, Antonov VE, Bazhenov AV, Bdikin IK, Borisenko DN, Krinichnaya EP, et al. Thermally stable hydrogen compounds obtained under high pressure on the basis of carbon nanotubes and nanofibres. Zh Eksp Teor Fiz Pisma 2004;79(5):280–5. http://dx.doi.org/10.1134/1.1753421. [Engl. Trans. JETP Lett. 2004; 79(5):226–230].

[28] Kuzovnikov MA, Tkacz M. Dihydride formation in the palladium–rhodium alloys under high hydrogen pressure. Int J Hydrogen Energy 2017;42(1):340–6. http://dx.doi.org/10.1016/j.ijhydene.2016.11.133.

[29] Salles V, Bernard S. A review on the preparation of borazine-derived boron nitride nanoparticles and nanopolyhedrons by spray-pyrolysis and annealing process. Nanomater Nanotechnol 2016;6:1–13. http://dx.doi.org/10.5772/62161.