

Superconductivity in compressed hydrogen-rich materials: pressing on hydrogen.

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Periodic table of elements starts with Hydrogen, a simplest element of all. The simplicity is lost when the element is compressed to high densities or participates in a chemical bonding in compounds, being subjected to “chemical pressure” of surrounding atoms or molecules. The chemical nature of hydrogen is dictated by its simplest electronic shell, which has only one electron. Hydrogen can donate this electron and behave like alkali metal, or accept an extra electron and form a hydride ion with closed shell resembling a group VII element. The complexity of hydrogen goes beyond these simplest configurations, when hydrogen is involved in a multicenter bonding or in hydrogen bonds. This complex behavior is tightly related to the ability of hydrogen to participate in the process of electronic transport in solids and potentially be able to contribute to the superconductivity in a material. Hydrogen by itself when compressed to immense pressures of 400-500 GPa may form a simple atomic phase with very high critical superconducting temperatures (T_c) well above room temperature. While this theoretical insight awaits confirmation at pressures at the limit of current experimental capabilities, a variety of other hydrogen-rich materials have been suggested recently to have record high T_c values. The very existence of many of these materials still lacks experimental confirmation. In this review article, we will present an extensive list of such predicted materials. We will also review superconductivity in classical hydrides (mostly metal hydrides) and current theoretical understanding of relatively low T_c 's in metal hydrides of transition and noble metals.

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Article outline

- 1. Introduction**
- 2. Phonon-driven superconductivity in hydrides**
 - A. Electron-phonon coupling and anharmonic effects**
 - B. Anharmonic reduction of T_c : PdH, PtH.**
- 3. Hydrogen “doping“ with other elements**
 - A. Silane and its siblings**
 - B. Polyhydrides of alkali and alkaline earth metals**
- 4. Prospects for room temperature superconductor based on hydrogen-rich materials: concluding remarks**
- 5. Appendix: Properties of the superconducting state of hydrides**

Introduction

As we may expect, chemical nature of hydrogen dictates its participation in transport phenomena in solids. “Dual” nature of hydrogen as an electron donor or acceptor, and its tendency to form multicenter bonds of various degree of complexity (1), provides for a variety of chemical environments for hydrogen (2). While “ionic” character of a hydride ion or a proton in most of these environments (3) is leading to insulating properties, a multicenter or metallic bonding (1) promotes materials with metallic conductivity. Within a BCS (Bardeen, Cooper and Schrieffer) scenario of superconductivity (4) high vibrational frequencies of hydrogen atoms raised hopes (5) for a high critical temperature in conducting hydrogen and hydrogen-rich materials (6). However, multiple attempts to find a material with high critical superconducting temperature in hydrides of transition and rare-earth metals did not produce a high- T_c material. The highest T_c 's observed in hydrides of Pd and Pd-Au, Pd-Cu alloys did not exceed temperatures of the order of 15-17 K (7, 8). Moreover, substantial inverse isotope effect was observed in PdH and PdD, at first raising doubts in the validity of the electron-phonon coupling mechanism for superconductivity in these materials, and later leading to the understanding of the role played by anharmonicity of hydrogen vibrations in such “simple” hydrides (9). It should be noted that there are published claims of nearly room-temperature superconductivity in PdH_x materials (10), which have not been confirmed by other experimentalists and have no theoretical backing at the moment.

The ability to create hydrogen-based materials with desired properties has received tremendous boost recently from a variety of government funded programs aimed at a viable hydrogen storage material for automotive and energy-storage related applications

(11, 12). Chemical compounds (11), weakly interacting molecular materials (12, 13), surface interactions (14) have been attempted with limited success to conveniently store and retrieve hydrogen. However, no practical material for hydrogen storage did emerge from this massive effort so far. Despite the deceptive simplicity hydrogen turned out extremely complex chemical entity as a component of useful materials. The properties of hydrogen in high-pressure environment become even more complex. High energy density (15), high-temperature superconductivity and superfluidity (16) are expected in dense hydrogen and hydrides. Ambient pressure metastable metallic phase of hydrogen, consisting of weakly interacting chains of hydrogen atoms with interatomic distances about 1.06 Å was predicted in 1970's by Brovman and Kagan (17). Ashcroft (6) proposed a metallic state in hydrogen-rich alloys, where the electronic bands of hydrogen and the host element(s) overlap. In the work that followed, the superconductivity was found with T_c approaching 20 K in transport measurements performed by Eremets et al. (18). This claim was subjected to experimental (and theoretical) scrutiny as discussed in section 2 of this review. As a development of this idea, very unusual metallic polyhydrides of lithium have been proposed (19, 20) to exist at pressures about 100 GPa, well below the expected metallization pressure of pure hydrogen (21). Stable polyhydrides of alkali metals have been predicted recently by theoretical analysis of MHn (M= Li, Na, K, Rb, Cs) compounds with variable hydrogen composition (19, 20, 22-25). These alkali and alkali earth polyhydrides will be reviewed in section 3.

Finally, we will discuss the prospects for high- T_c hydrogen-rich materials in a high-pressure environment. Both theoretical insights and experimental challenges will be discussed.

2. Phonon-driven superconductivity in hydrides

A. Electron-phonon coupling and anharmonic effects

We give below a quick summary of the results for electron-phonon coupling driven superconductivity relevant for the discussion of hydrogen-based superconductors. The critical superconducting temperature for a phonon-mediated superconductor can be conveniently represented by modified McMillan formula (26, 27) :

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right] \quad (1)$$

where ω_{\log} is a logarithmic average of the phonon frequency, λ is electron-phonon coupling constant, and μ^* is the Coulomb pseudopotential of Morel and Anderson (28).

Another useful formula is defining electron phonon coupling parameter λ

$$\lambda \equiv \frac{N(\epsilon_F) \alpha^2}{M \omega_E^2} \quad (2)$$

in terms of the density of the electronic states $N(E_F)$ at the Fermi level, the phonon frequency ω_E and effective mass M , and the Holstein parameter α , a Fermi surface average of the electronic matrix element of the change in crystal potential as particular phonon mode-related atoms are moved (26). Partial contribution of phonon modes was analyzed in (29) for weakly coupled phonons; we show a figure with the results of this analysis (Fig.1)

$$\frac{1}{E} \frac{\delta T_c}{\delta \alpha^2(\Omega) F(\Omega)} \quad 101$$

$$\frac{\delta T_c}{\alpha^2(\Omega) F(\Omega)} \equiv \lim_{\epsilon \rightarrow 0} \frac{\delta T_c}{\epsilon} = \frac{1}{1 + \lambda} G(\bar{\Omega}) \quad (21)$$

where

Fig.1. Function $G(\bar{\Omega})$, $\bar{\Omega} = \Omega/T_c$ is the reduced frequency ($\hbar=1$, $k_B=1$). Reproduced from Solid State Commun. from Mitrović and Carbotte (29).

Fig.1 shows relative partial derivative of the T_c with respect to small change in the partial coupling strength $\alpha^2(\Omega)F(\Omega)$ at phonon frequency Ω , with broad maximum around $\Omega=10$. It means that the phonon frequencies contributing mostly to T_c , are about factor of 10 higher in frequency than the T_c (in equivalent units, $\hbar\omega/k_B T_c$). This result along with Eq.1, strongly favors high vibrational frequencies as a prerequisite of high T_c values. The highest vibrational frequencies are found in hydrogen in hydrides; for this reason hydrogen-rich materials have attracted significant amount of attention in the search for highest T_c values in materials. However, historically the quest for high- T_c hydrogen based materials did not produce any significant results. The early era before high- T_c cuprates, was reviewed in (30). Despite significant effort, only two families of relatively high T_c materials have been found with Th (31) and Pd (7, 32) hydrides. Both systems showed anomalous isotope effect when doped with deuterium; $\text{ThH}(\text{D})_{3.64}$ did not show any isotope effect, which initially raised doubts regarding the phonon-mediated mechanism, and $\text{PdH}(\text{D})$ showed inverse isotope effect (9). In the theoretical and

experimental papers that followed discovery of PdH superconductor, the anomalous isotope effect was understood as resulting from anomalously large anharmonicity of hydrogen (deuterium) vibrations (33, 34, 35-37). While earlier works used empirically scaled experimental phonon spectrum (34), the latest theoretical efforts have explained the observed anharmonicity from the first principles (37). Since the anharmonic effects are not treated explicitly in lately predicted high- T_c 's in transition and noble metal hydrides (38, 39), we will give a brief overview of current understanding of the anharmonicity effects on T_c in these materials.

1.B Anharmonic reduction of T_c : PdH, PtH.

In the early paper Klein et. al. (34) have used the measured phonon densities of states in PdH(D) (40) to introduce semiempirical correction to the electron-phonon coupling constant, and they concluded that observed (quartic) anharmonicity is sufficient to explain the anomalous isotope effect. Similar considerations were used in several other theoretical approaches; Klein and Cohen have calculated the phonon spectra and were able to reproduce the inverse isotope effect qualitatively (41). They also noticed strong dependence of the isotope effect on Coulomb pseudopotential (Eq. 1), which is theoretically justified (42). Anharmonic vibrations of hydrogen in AlH₃ were suggested (43) as the reason for disagreement between “harmonic” calculation and experimental findings (44). In Fig. 2 we show highly anharmonic character of hydrogen vibrations (quartic anharmonicity) as follows from the frozen-phonon calculations (43).

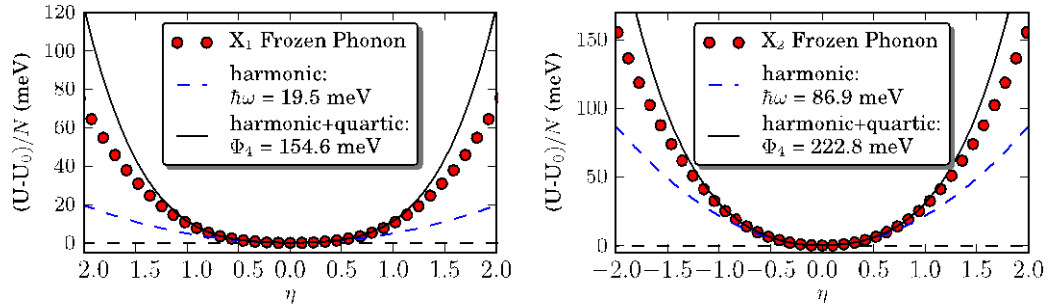


Fig.2. Frozen phonon total-energy calculations for the modes at X with frequencies ~ 20 meV (X1) and ~ 85 meV (X2), as a function of a displacement parameter η . Reproduced from Physical Review B (43).

Recently, Erea et al. (37) have performed ab-initio calculations of T_c in PdH using newly developed Stochastic Self-Consistent Harmonic approximation (SSCHA) – see also Ref. (45). This work was followed by two papers demonstrating the effect of anharmonicity on calculated T_c in PtH and PdH (45), and in other hydrides and chalcogenides (46). Their results show that the harmonic approximation describing the vibrations of atoms in solids can completely break down when the displacements of the atoms exceed the range in which the harmonic potential is valid. Such situations occur mostly for very light atoms like hydrogen, or in very soft effective potentials (47). In Fig.2 we reproduce the electron-phonon coupling calculation for PtH from Erea et al. (45).

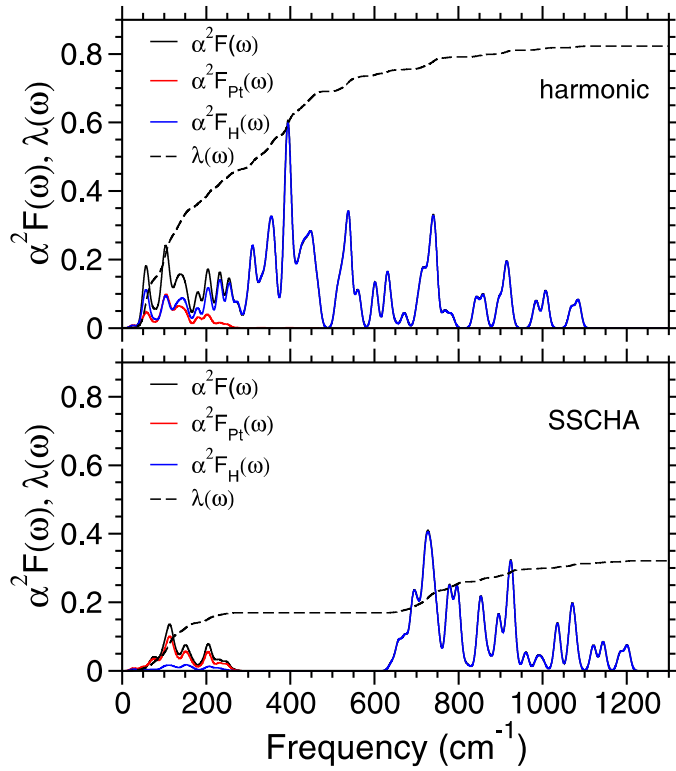


Fig.3. $\alpha^2 F(\omega)$ and $\lambda(\omega)$ of PtH at 100 GPa and 0 K in the harmonic approximation (top) and in the SSCHA (bottom). The contribution of Pt and H atoms to $\alpha^2 F(\omega)$ is also shown. Reproduced from Phys. Rev. B., Erea et. al. (45).

As is clear from Fig. 2, the calculations in SSCHA formalism, taking account of anharmonic effects, reduce significantly theoretical estimation of electron-phonon coupling contribution due to vibrations of hydrogen atoms. The calculated anharmonic hydrogen vibrations are located much higher in frequency, than harmonic approximation would predict. According to Fig.1, the contribution to the T_c should dramatically decrease, since the phonon density of states is shifted by more than factor of 10 above the energy corresponding to T_c .

3. Hydrogen “doped“ with other elements

A. Silane and its siblings

The possibility that compressed hydrogen may convert to a metallic state under compression was first suggested in 1935 (48), but experimental realization of metallic hydrogen in its solid atomic form (49) remains a challenging goal. In 2004, Ashcroft suggested that dense hydrides of group IVa elements are promising candidates for realizing metallization of solid hydrogen at pressures considerably lower than may be necessary for solid hydrogen because hydrogen has already undergone a form of “chemical pre-compression” (6). The idea of diluting hydrogen with other elements is not new (50), but only recently experimental x-ray, Raman, transport, and infrared measurements as well as theoretical calculations have been performed on the group IVa hydrides (mostly silane SiH_4 and germane GeH_4) in order to explore their metallization and potential superconductivity suggested by Ashcroft(6). Experimental (51) and theoretical (52) results pointed to instability of germane at high pressures and even enabled measurements of high-quality x-ray diffraction data on high-pressure germanium phases (51), which were possible due to perfect powder x-ray diffraction of germanium in a soft pressure medium (H_2) formed by decomposition of GeH_4 .

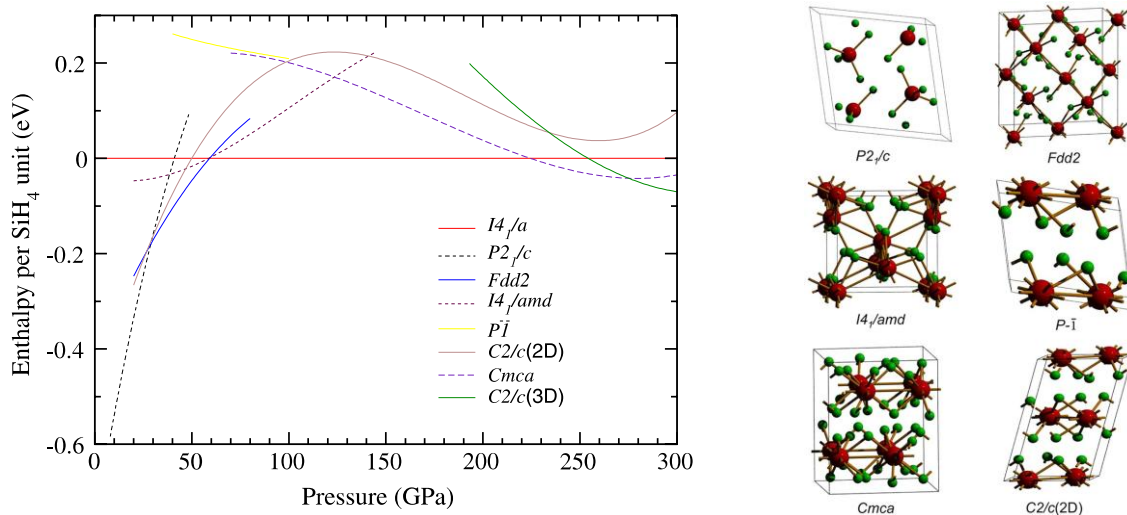


Fig.4. The enthalpy versus pressure for competitive structures of SiH₄. The enthalpy of the I4_{1/a} phase is taken as the reference point. The “enthalpically” most favorable structures computed for SiH₄ polymorphs at high pressures are shown on the right (53). The Cmca structure having a layered network is the most likely candidate of the metallic phase of SiH₄ over a wide pressure range above 60 GPa. The superconducting transition temperature in this layered metallic phase is found to be in the range of 20–75 K (53).

The early theoretical work on silane (54-56) initiated significant experimental and theoretical efforts in search for superconductivity. Silane (SiH₄) has been the subject of several recent high-pressure studies. Chen et al. (57) used high-pressure spectroscopy to identify high-pressure behavior of silane. They found from Raman spectroscopy one fluid-solid transition at around 4.0 GPa and three solid-solid transitions near 6.5 GPa, 10 GPa, and 26.5 GPa at room temperature. Four high-pressure solid phases were detected, which we named phase III, IV, V, and VI. The infrared results show an increase of the reflectivity starting at 60 GPa (57), pointing at pressure-induced metallization, which confirms the prediction by Ashcroft (6). The results indicated that SiH₄ is a good candidate for the realization of the metallization of hydrogen under pressure. Theoretical

predictions by Chen et al. also favored high pressure superconductivity in silane (53) – see Fig.4. The predictions were made by other groups (58-60), also indicating high pressure superconductivity in silane. Indeed, the superconductivity was found with T_c approaching 20 K in transport measurements performed by Eremets et al. (18) – Fig.5. While silane remains stable below 50 GPa (61), it was claimed that it decomposes above 50 GPa (62) forming pure silicon (Si) and hydrogen (H_2), which in turn reacts with the metallic gasket (Re) or electrical leads (Pt) and may be responsible for a superconductivity and x-ray diffraction from platinum hydride observed in experiments by Eremets (18) and attributed to metallic silane. Further experiments by Hanfland et al. pointed to amorphisation of silane at 60 GPa and to formation of polymeric silane around 100 GPa (63). This study also found that silicon and hydrogen react above 100 GPa to form stable polymeric phases of silane (63). In the absence of decomposition, silane was found to remain partially transparent and nonmetallic to at least 150 GPa with a band gap constrained between 0.6 and 1.8 eV (64).

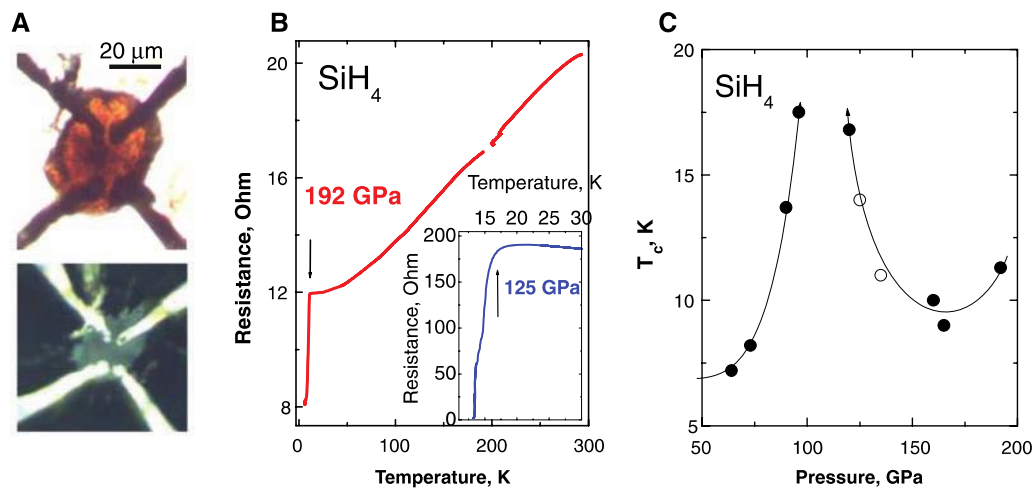


Fig.5. Electrical resistance and superconductivity in silane. (A) Photographs of silane at 125 GPa taken in transmitted (above) and reflected (below) light after annealing at $T = 400^\circ\text{C}$. Silane is transparent at this pressure; nevertheless, it noticeably reflects light. (B) A representative superconducting step on the

temperature dependence of resistance of silane at 192 GPa and 125 GPa (inset). Arrows indicate T_c . Electrical measurements were performed before the annealing, when an essential part of the sample remained in the metallic phase. (C) Pressure dependence of the critical transition temperature T_c of silane. Reproduced from Science (18).

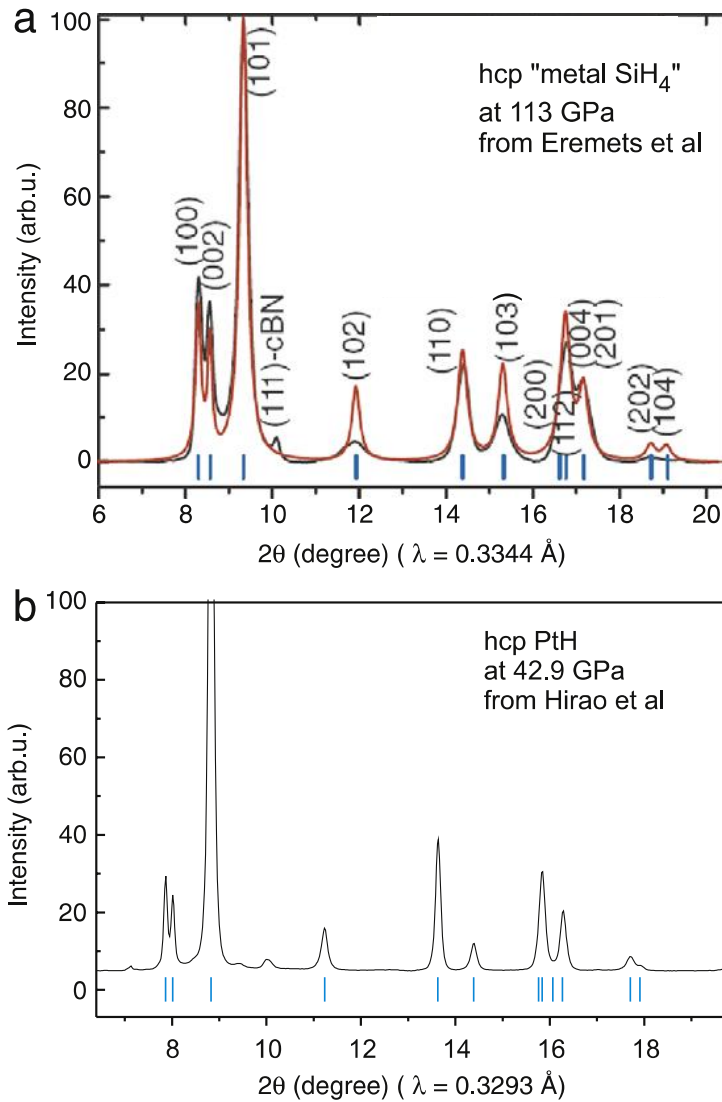


Fig.6. SiH₄ - PtH controversy. Powder diffraction spectra of (a) the claimed “hcp phase of metallic silane” (18) and (b) hcp phase of PtH synthesized at high pressure. The tick marks in (b) show peak positions calculated from the reported lattice parameters for PtH in its hcp phase: $a = 2.773(1) \text{ \AA}$, and $c = 4.713(1) \text{ \AA}$. reproduced from Solid State Communications, Degtyareva et al. (62).

Experimentally, controversies regarding the decomposition of silane at high compression and its superconductivity are not resolved yet – Fig.6. We have performed both resistivity and magnetic susceptibility experiments (65) in platinum hydride formed in situ at high pressure to check the suggested effect (62) of electrical leads in previous experiments on silane (18). We were not able to confirm superconductivity of platinum hydride up to 100 GPa. Further magnetic susceptibility experiments may be required with silane loaded in a gold-lined and cBN gasket to exclude the effect of a metallic gasket and to contain possibly released hydrogen. In view of the theoretical results on anharmonic suppression of T_c in PtH, the high T_c observed in (18) may belong to superconducting phases of SiH_x compounds with different stoichiometry (66-69) or to polymeric phases of silane (63).

Stannane (SnH_4) (60) and plumbane (PbH_4) (70) were proposed as high-pressure (high-temperature) superconductor (SnH_4) and liquid metal (PbH_4), but experimental attempts to create these compounds at high pressure have not been reported so far.

B. Polyhydrides of alkali and alkaline earth metals

The content of this section will cover exclusively recent theoretical developments, which are very new and mostly did not find experimental confirmation at his moment. However, experiments are underway and experimentalists would benefit from a concise review of predicted polyhydrides, which have unusual compositions and defy our intuitive expectations.

As a very first development in that direction, metallic polyhydrides of lithium have been proposed (19, 20) to exist at pressures above 100 GPa, well below the expected metallization pressure of pure hydrogen (21). Stable polyhydrides of other alkali metals have been predicted recently by theoretical analysis of MH_n ($M = \text{Li, Na, K, Rb, Cs}$) compounds with variable hydrogen composition (19, 20, 22-25). The compounds with $n \geq 2$ are expected to become stable at pressures as low as few GPa in the case of Cs and above 100 GPa in the case of Li.

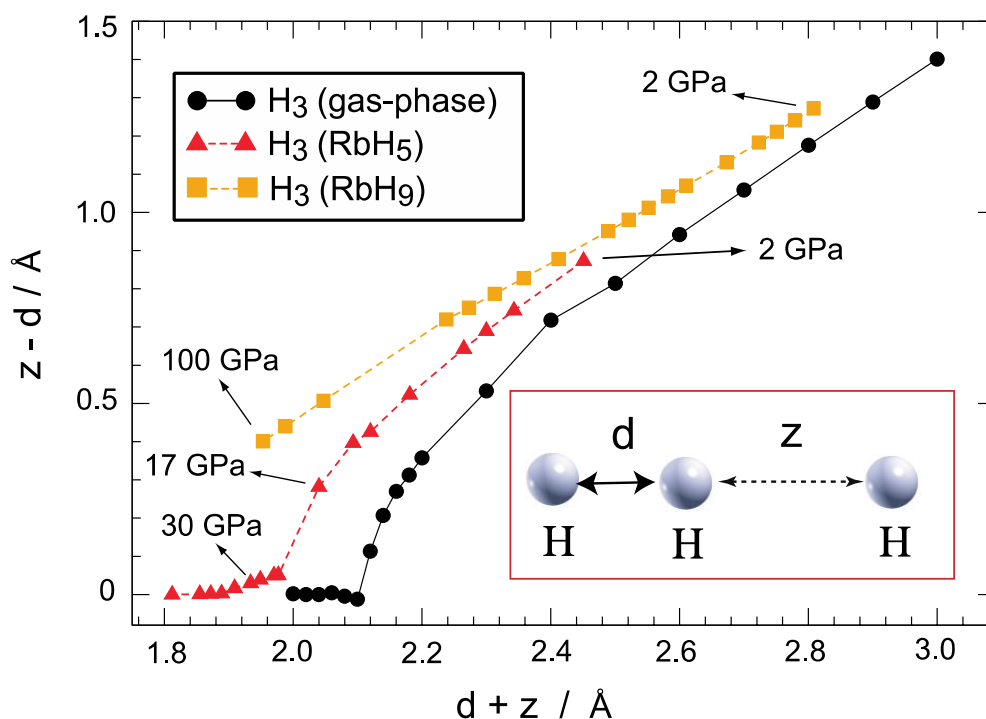


Fig. 7. The difference between the z and d distances in an $H-\cdots H_2$ fragment (see inset) is plotted vs. their sum for an isolated H_3^- molecule in the gas phase. During the optimization, the total length of the molecule was constrained and the central atom was allowed to relax freely. These values are also illustrated for an $H-\cdots H_2$ unit in $lp\text{-RbH}_9$ and $lp\text{-RbH}_5$. Reproduced from Chem. Eur. J., Hooper et al. (71).

New polyhydride phases are also anticipated for alkaline earth metals (24, 72, 73). The theoretically predicted polyhydrides are not only stabilized by compression, but are expected to metalize and exhibit superconducting properties at lower pressures than the constituent parts--the monohydride and hydrogen. Critical superconducting temperatures as high as 235 K have been predicted for polyhydrides of Ca (72).

These compounds provide new chemical means to pre-compress hydrogen molecules and to facilitate the creation of metallic superconducting hydrogen (5) with record high critical superconducting temperatures. Notably, linear H_3^- ions were predicted to form in polyhydrides of softer alkali metals, for example in RbH_5 (71) and CsH_3 (25). Such H_3^- ions (see for example Fig. 7) have a tendency to be stabilized in a linear configuration, contrary to triangular-shaped H_3^+ ions (74, 75). Symmetric H_3^- ions with interatomic distance 1.06 Å and with the lowest potential barrier (76) were discussed as transition states in hydrogen exchange processes of metal complexes (77). H_3^- and D_3^- ions were experimentally observed in discharge plasmas only recently (78). The chains of H_3^- ions that were found theoretically in RbH_5 (25) and CsH_3 (71), resemble one-dimensional hydrogen chains of ambient pressure metastable metallic hydrogen phases predicted in 1976 by Browman and Kagan (17). Such chains were also extensively discussed as a simplest model of strong correlations in a linear chain of hydrogen atoms (79, 80). In recent paper, Grabowski and Hoffman (81) have considered stabilization effect of the excited state of H_3^- anion with hydrogen separation 0.93 Å on a $(LiHHHLi)^+$ pentaatomic cation and also found (81) a linear coordinated arrangement. Other local stable clusters have been proposed. The pure hydrogen clusters (H_3^+ , H_3^- , etc...) and

clusters of hydrogen with other elements (81) may serve as building blocks of pressure-induced metallic phases. We are only starting to develop our intuitive understanding of emerging new strongly compressed materials with unexpected chemistry and physical properties.

| | |
|----------------------------------|-------------------------------|
| LiH_2 LiH_6 | BeH_2 |
| NaH_3 NaH_7 | MgH_4 |
| NaH_9 NaH_{11} | MgH_{12} |
| KH_3 KH_5 | MgH_{16} |
| $\text{KH}_8 \dots$ | CaH_6 |
| RbH_3 RbH_5 | SrH_6 |
| CsH_3 CsH_7 | BaH_6 BaH_8 |
| $\text{CsH}_9 \dots$ | $\text{BaH}_{12} \dots$ |

| | |
|--------------|----------------|
| H_2 | |
| LiH | BeH_2 |
| NaH | MgH_2 |
| KH | CaH_2 |
| RbH | SrH_2 |
| CsH | BaH_2 |

| | | | | |
|------------------------|----------------|----------------|-----------------------|--------------|
| | | | H_2 | |
| B_2H_6 | CH_4 | NH_3 | H_2O | HF |
| AlH_3 | SiH_4 | PH_3 | H_2S | HCl |
| GaH_3 | GeH_4 | AsH_3 | H_2Se | HBr |
| | SnH_4 | SbH_3 | H_2Te | HI |
| | PbH_4 | BiH_3 | H_2Po | HAt |

Fig.8. The modified Periodic Table shows hydrides of the elements belonging to main groups. A separate block on the left summarizes a variety of polyhydrides predicted recently and discussed in this section. NaH_3 and NaH_7 were synthesized recently in our group (submitted).

Alkali and alkaline earth polyhydrides predicted recently are summarized in Fig. 8. Apparently, polyhydrides of other main group elements may exist, as was reported

recently, for example, in Xe (82). Group VII polyhydrides, if they exist, would be “hole doped”, as compared to alkali and alkaline earth, which are “electron doped”. We may expect very different properties for hole doped polyhydrides, and also quite different local arrangements, possibly based on triangular H_3^+ cation (75). In this review we did not discuss polyhydrides of transition metals or rare earth metals at high pressure, which have only limited impact in current literature (83) and have limited connection to high-pressure experiments at this time, with only one candidate for “non-interstitial hydride”, IrH_3 (84). Existing classical “interstitial” metal hydrides were briefly discussed in section 1.

As a concluding remark, despite a wealth of theoretically predicted high pressure polyhydride structures, none of the predictions have been confirmed experimentally until now in the published literature. Also, the claims of metallic and superconducting phases should be considered with caution, and further in-depth theoretical analysis of superconducting properties may be required.

We have tried to create polyhydrides of Li (without success, see also Ref. (85)) and Na (NaH_3 and NaH_7 synthesized, work in progress) (86). We are optimistic and are looking forward to new polyhydrides coming to life very soon.

Notes added. When this paper was in review, the paper by Drozdov et. al. was published reporting nearly 190 K conventional superconductivity in H_2S hydride at 200 GPa (87). The experimental procedure and theoretical results by Duan et. al. (88) suggest that observed high T_c values may correspond to a polyhydride H_3S phase forming at high pressures when the sample is warmed up to room temperature (87). The experiments have reported superconductivity from resistivity measurements. If these results will be

confirmed by magnetic susceptibility measurements, there will remain no doubt that conventional phonon driven conductivity is possible close to room temperature. It is interesting to note that hydrogen in H_3S and its homologues would represent a test case to study a long sought “hole doped” metallic hydrogen, as discussed in this section.

4. Prospects for room temperature superconductor based on hydrogen-rich materials: concluding remarks.

Current candidate materials for high-temperature or even room-temperature superconductivity were discussed at length in previous sections. However, none of the predicted materials matches pure hydrogen as a candidate for room temperature superconductivity – Fig. 9. Pure hydrogen remains in the focus of current research, and quite remarkable progress in bringing hydrogen to nearly 400 GPa has been reported recently (89-94).

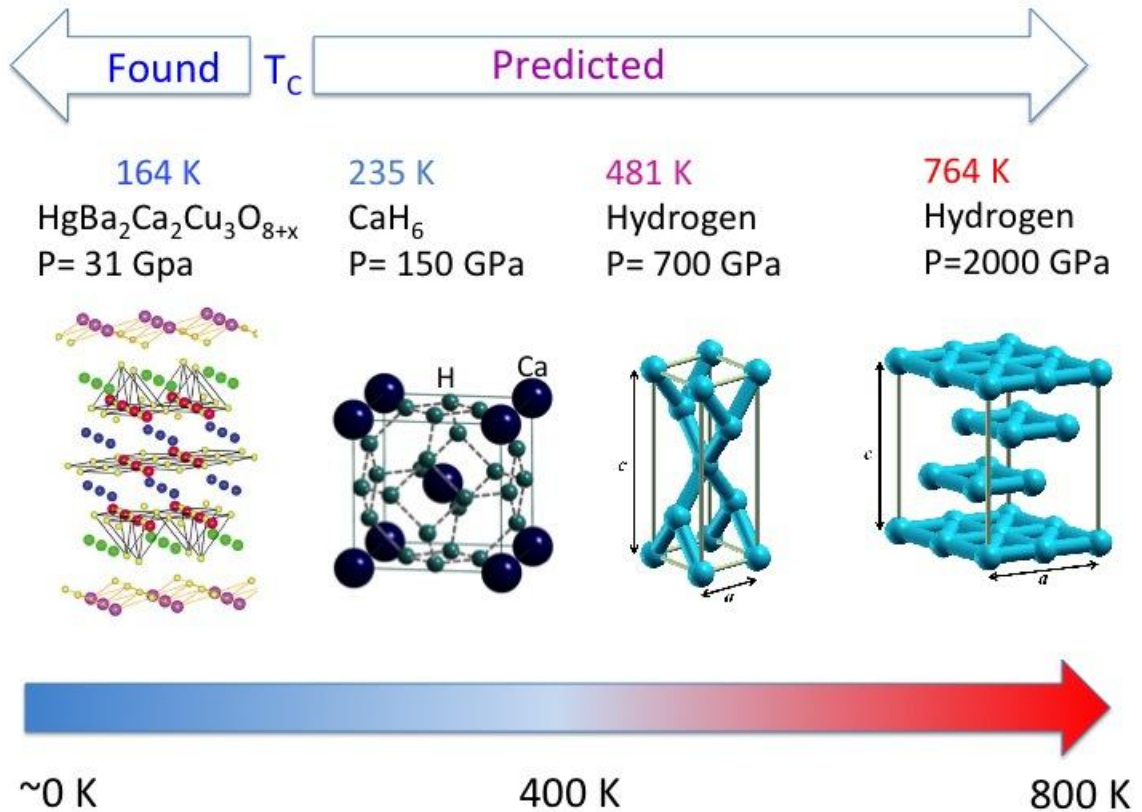


Fig.9. The highest T_c reached so far in a mercury based cuprate is 164 K at 30 GPa (95). T_c 's close to room temperature were predicted for CaH_6 at 150 GPa, and T_c 's well above room temperature are expected in metallic hydrogen (atomic form) (49). Recent claim of superconducting hydrogen sulfide (87) may change the record of the T_c to 190 K, if confirmed.

Conducting hydrogen has been claimed by Eremets and Troyan (96), however, this work has received a serious criticism (97). If this experiment will stand the test of time, it has reported semimetallic, poorly conducting molecular phase of hydrogen (97). It should be noted here that high T_c 's were also predicted in metallic molecular forms of hydrogen - see (98, 99) and references therein.

Apparently, room temperature superconducting atomic hydrogen (49) is still on the radar for experimentalists. Experimental challenges are significant, but the task of

reaching the immense pressures required to metalize hydrogen may be facilitated by recently developed double-stage diamond anvil technique (100). A combination of such technique with precise photolithography or Focused Ion Beam (FIB) techniques (101) may help to manufacture tiny electrical leads in a double-stage diamond anvil cell (DAC) and to probe metallization of hydrogen above 400 GPa.

New predicted polyhydrides (section 3) also hold a great promise to have high critical superconducting temperatures. However, predicted high T_c values should be carefully checked both by experiment and by more accurate calculations taking account of anharmonic effects. In view of recently reported superconductivity with $T_c \sim 190$ K in hydrogen sulfide (87), the “hole doped” hydrogen in combination with chalcogens or pnictides, or both, is a promising chemical route to new high- T_c superconducting materials.

5. Appendix: Properties of the superconducting state of hydrides

Table 1. The properties of hydride materials available in the literature, such as critical fields (H_{c1} and H_{c2}), pressure effect on the T_c , superconducting gap, isotope effects, and other available information, are listed along with the references to original publications. The information available for metal hydrides is limited due to difficulties in growing stoichiometric samples. This may also explain a large scatter in experimentally measured parameters. The information for PdH(D) and ThH(D) is dominant due to the large interest to the inverse isotope effect in these hydrides and their enhanced T_c values.

It should be also noted that hydrides of many transition and rare earth metals have been studied but no superconductivity has been found in them – see e. g. Refs. (30), (102)

for a list of such hydrides. Many examples are also given (30) showing that small amounts of hydrogen dissolved in a superconducting metal usually suppress its T_c .

| Hydride | T_c (K) | Properties of the superconducting state | Reference |
|---------------------------------|--|---|--------------|
| H ₂ S | 30-150 | P from 110 GPa to 200 GPa | (87), (103), |
| D ₂ S | 20-50 | P from 100 GPa to 175 GPa | |
| H _x S | 160-190 | P from 150 to 200 GPa , possible x=3 | (88) |
| D _x S | 90 | P=170 GPa | |
| H ₂ S | 60 | H_{c2} = 25 T | |
| H _x S | 185 | H_{c2} = 72 T | |
| SiH ₄ | 17.5 | at P~100 GPa | (18) |
| PdH _{0.97} | 8.3 | H_{c2} = 1.7 T | (104) |
| PdH _{0.97} | 6.6 | H_{c2} = 0.18 T | (105) |
| PdH _{0.996} | 10.4 | H_{c2} = 0.09 T | (106) |
| PdH _x | 3.4 3.6 4.2 5.5 6.2 7.7 | H_{c2} (T) dH_{c2}/dT (T/K) $\rho_n(10^{-5} \Omega \text{ cm})$ 0.219 0.0645 1.23 0.238 0.0660 1.27 0.252 0.0600 1.04 0.250 0.0455 0.85 0.218 0.0350 0.61 0.243 0.0315 0.60 ρ_n - residual resistance | (107) |
| PdD _{0.9} | 5.5 | $2\Delta_0/k_B T_c = 3.6$ | (108) |
| PdH _x | 4.6 | $2\Delta_0/k_B T_c = 3.8$ | (109) |
| PdH _x | 4.6 | $2\Delta_0/k_B T_c = 2.6$ | (110) |
| PdH | 8.8 | $d\ln T_c/dP = -6.8 \cdot 10^{-3} \text{ kbar}^{-1}$ | (111) |
| PdD | 11.05 | $d\ln T_c/dP = -5.0 \cdot 10^{-3} \text{ kbar}^{-1}$ | |
| Th ₄ H ₁₅ | 8.3 | $H_{c2} = 2.5-3.0 \text{ T}$ | (31) |
| Th ₄ D ₁₅ | 8.3 | $H_{c2} = 2.5-3.0 \text{ T}$ | |
| Th ₄ H ₁₅ | 7.62 | $d\ln T_c/dP = 5.5 \cdot 10^{-3} \text{ kbar}^{-1}$ | (112) |
| Th ₄ H ₁₅ | 7.9 | $2\Delta_0/k_B T_c = 3.42$ | (113) |
| Th ₄ D ₁₅ | 7.9 | $2\Delta_0/k_B T_c = 3.47$ | |
| Th ₄ H ₁₅ | 7.97 | $\Theta_D = 211.5 \text{ K}$, $\gamma = 8.07 \text{ mJ} \cdot \text{K}^{-2} / \text{mole Th}$ | (113) |
| Th ₄ D ₁₅ | 8.00 | $\Theta_D = 216.5 \text{ K}$, $\gamma = 7.84 \text{ mJ} \cdot \text{K}^{-2} / \text{mole Th}$ | |
| MoH _{1.27} | 0.92 | $H_c = 60 \text{ mT}$ | (114) |
| MoD _{1.26} | 1.4 | $H_c = 30 \text{ mT}$ | |

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