

Metallization and superconductivity of hydrides under high pressure

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Abstract

Hydrogen, the lightest and the most abundant element in the universe becomes a mainstay of contemporary condensed matter physics, which is largely because its metallization is regarded as the holy grail of high-pressure physics and it is also due to recent observations of high T_c superconductivity in hydrogen-dense compounds at extremely high pressure. Contemporary static high-pressure technique is not enough to realize the metallization of solid hydrogen and hydrogen-dense compounds may significantly reduce the required transition pressure providing an excellent proxy study. In this brief review, I will introduce recent achievements of high-pressure study in solid hydrogen and hydrides.

Keywords: hydrogen, hydride, pressure, metallization, superconductivity

1. Hydrogen under extreme conditions

Hydrogen, the simplest and lightest element in the periodic table consisting of one proton and one electron, becomes one of important research topic in contemporary science. At atmosphere, it exists as a gas of diatomic molecules (H_2) and if it can be isolated in the universe, it is also known that it can form a trihydrogen cationic molecule (H_3^+). There are also a few experimental reports of formation of H_3^- with very short lifetime when heavy ions collide with foils of metal hydrides [1, 2] where H_3^- consists of linear array of three hydrogen atoms. Theoretically their geometry was explained as electron-rich and electron-poor three centering bondings in extreme conditions [3] and these concept can be extended to formation of hydrogen polymers which were suggested theoretically by calculating their stability [4]. Even intriguing phase transitions in infinite hydrogen chain was proposed [5]. However, at standard conditions their stability seem to be marginal and they are recovered spontaneously to H_2 molecules.

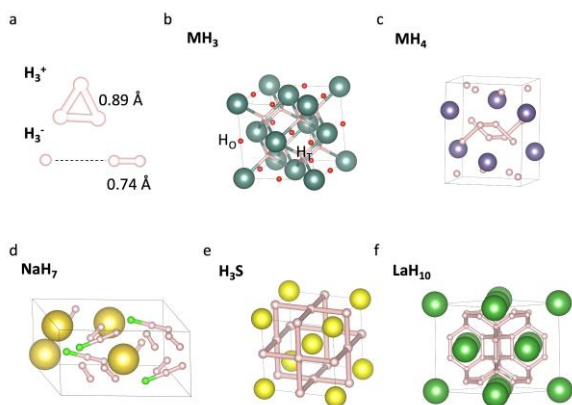


Fig. 1. computational predicted structures of hydrogen molecules and representative hydrides reviewed in this paper a) geometry of trihydrogen cationic molecule and anionic molecule b) cubic structured metal hydrides $M(H_T)_2H_O$ where two hydrogen sites occupy tetrahedral sites (pink) and one occupies octahedral site (red). Thus in this class of metal hydrides, monohydrides forms MH_O , dihydrides forms $M(H_T)_2$ c) tetrahydride with double hydrogen layers sandwiching single metal layer d) sodium polyhydride (NaH_7) with H_3^- substructure where the third hydrogen weakly bonded to H_2 is in green color e) experimentally observed cubic H_3S f) experimentally observed cubic LaH_{10}

Searching for monoatomic hydrogen (i. e. breaking H_2) has been conducted extensively. Dissociation of hydrogen molecule was attempted along temperature dimension by I. Langmuir [6] up to near 3100 K and showed that extremely high-temperatures are needed to initiate the reaction. Later, a seminal work by E. Wigner & B. Huntington suggested a concept of high-pressure induced metallization of hydrogen solid where they calculated total energy of body centered metallic hydrogen with respect to lattice constant change and found that pressure of 25 GPa can induce metallic modification [7]. In the paper, they also acknowledged their hypothetical structure may not be correct and other metallic phases may be energetically stabilized. However, they could not test their assumption because the required pressure was much beyond experimental limit.

Contemporary diamond anvil cell (DAC) technique enables to test Wigner-Huntington transition of hydrogen in experiment at extremely high-pressure. However, due to small size of sample and large band-gap nature, majority experiments used vibrational spectroscopy to track frequency change of H_2 vibron, instead of direct measurement of the band-gap. Raman measurement up to 63 GPa found no metallic modification but they found softening of molecular bond starting from ~ 30 GPa, which implies strongly interacting H_2 solid and possible

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dissociation of H_2 molecule once one extrapolates the trend to higher pressure [8]. To our best knowledge, there is no clear evidence of metallization of solid hydrogen while there are claims of observations [9]. The difficulty is that molecular-to-monoatomic transition of solid hydrogen comes from a strong electron-phonon coupling, namely Peierls distortion of hydrogen lattice, which distorts its electronic band structure to open the gap with a magnitude of ~ 14 eV [10]. Upon pressure the bandgap of molecular solid hydrogen monotonically decreases [11]. One needs to put equivalent external energy (~ 14 eV) to the system to restore hydrogen's monoatomic array. Pressure is only one thermodynamic variable that can deliver such a huge energy to the system, while other thermodynamic variable, for example temperature, can deliver energy up to melting point in the order of sub-electron volts [12]. One of most recent works reported that they observed a Wigner-Huntington transition near 500 GPa [13] by showing optical appearance change of the sample as evidence of the transition and Raman frequency to justify the unusually high pressure, which was immediately questioned by several groups [14-17]. Follow-up studies to cross-check the experimental data including measuring superconductivity should be done.

Theoretically, metallization of solid hydrogen was predicted to result in high- T_c superconductivity [18]. Suppose solid hydrogen becomes monoatomic solid, it will be a Drude-type good conductor as other alkali metal and it possesses the highest Debye temperature. Thus, one can easily expect very high superconductivity transition temperature, compared with other BCS-type superconductors.

Computational condensed matter approaches greatly contribute to prove the prediction in two ways. First, linear response calculations based on density functional theory was enabled and superconductivity T_c can be estimated by direct electron-phonon coupling calculations for complex materials. Actually, T_c was calculated for solid hydrogen to be very high as much as ~ 356 K near 500 GPa and up to 764 K at multi TPa [19]. Second, computational structure searching strategies combined with DFT make it possible to predict phases of solid hydrogen at various pressure range [20] and calculate the corresponding electronic structure of interest predicting electronic structure predictions such as semi-metallic transition of solid hydrogen [21].

2. Hydrides under high pressure

Experimental realization of metallic hydrogen is still elusive and N. W. Ashcroft suggested an alternative route, which utilizes *chemical pressure* to reduce required transition pressure [22]. If hydrogen forms compounds with heavy elements, for example in metal hydrides, valence electrons of metal atoms are transferred to hydrogen sublattice providing a proxy study of hydrogen solid with excessive electrons. The extra electrons sit at antibonding states of H_2 and weaken the covalent bonding strength, which accordingly reduce the required transition

pressure of H_2 dissociation. Ideally, in this case, hydrogen forms sublattice with a finite electron density at the Fermi level dominating conductivity in hydrides.

Searching high- T_c hydrides has been studied in experiments starting from Th_4H_{15} [23] and PdH_x [24] in 1970s. In this euphoric period to search new hydride superconductors, lanthanides hydrides are also searched extensively to find a high- T_c superconductor, which results in a finding of other phenomena such as a metal-insulator transition, namely switchable mirror phenomenon in yttrium hydrides [25]. However, these systems mostly consist of direct metal-hydrogen bondings and thus high Debye temperature is unlikely expected.

Silane (SiH_4) was one of important examples as it is a typical hydrogen-dense compound suggested by N. W. Ashcroft in his seminal work [22]. In 2008, two consecutive papers were published reporting an observation of insulator-to-metal transition at 60 GPa [26] and superconductivity at 60-200 GPa [27], respectively. Interestingly, reported T_c data show a diverse shape near 100 GPa and stimulated many following-up studies. However, independent experiment found no metallic phase up to 124 GPa and 300 K [28], which is also consistent to a theoretical prediction [29].

Alternative scenario of the observed superconductivity in the literature [27] was theoretically suggested where pressure induced platinum hydride formation and the associated superconductivity transition were predicted [30]. Pt was used as an electrode in SiH_4 experiment and at relatively low pressure, SiH_4 is subject to dissociation and release hydrogen that may react with Pt electrodes. Later, experimental observation of superconductivity in hexagonal structured PtH_x was reported [31]. It should be also noted that, amorphous silicon and other silicon hydrides under pressure were reported to be superconductors [32] and thus the clear understanding of experimentally observed superconductivity is still inconclusive.

At lower pressure, lanthanides hydrides shares a prototype structure which is cubic MH_3 where two hydrogen atoms occupies tetrahedral sites (H_T) and one hydrogen sits at octahedral site (H_O). monohydride has cubic MH_O , $M(H_T)_2$ forms a dihydride and finally $MH_O(H_T)_2$ completes trihydrides. There is a tendency that hydrogen concentration increases with increasing pressure in these metal hydrides [33] and general trend of superconductivity of these hydrides was predicted [34]. With increasing pressure, theoretically several tetrahydrides (MH_4) have been predicted and interestingly they commonly possess a layered structure where M and H are separated, and hydrogen-layers conducts mainly. Thus, we can expect high Debye temperature and the corresponding high T_c in hydrogen layer. Also, we can speculate that higher hydrogen concentration requires higher transition pressure and the expected T_c is also higher as theoretically suggested [34].

To pursue higher T_c hydrides synthesis, experimental efforts to stabilize polyhydrides have been conducted. In 2009, M. Somayazulu et al. reported a formation of hydrogen-rich Xe- H_2 compounds starting 4.8 GPa [35] and

T. A. Strobel et al. found $\text{SiH}_4(\text{H}_2)_2$ compound below 10 GPa [36]. In these hydrides H_2 molecules are bound to heavy element very weakly and thus they do not contribute to conductivity. Under pressure (~ 40 GPa), sodium polyhydrides over the well-known ionic sodium monohydride were formed and especially a formation of NaH_7 was reported where H_3^- unit identified from unusual Raman signal [37]. Formation of RuH_4 at 85 GPa was reported and its semi-metallic bandstructure was also predicted [38]. An experimental measurement of superconductivity in polyhydrides was recently reported for ionic salt BaReH_9 [39]. In their report they used laser heating to accelerate the transition at 100 GPa and found a superconductivity transition near 7K. In BaReH_9 , hydrogen also directly form a bonding with nearest heavy elements and does not form a conducting hydrogen sublattice.

Hydride research moves to higher pressure much beyond 1 megabar (100 GPa) and eventually reports high- T_c hydrides, proving theoretical prediction by N. W. Ashcroft. H_2S is a colorless chalcogen hydride gas at ambient conditions and at high pressure H_3S becomes stabilized with a cubic structure possessing conducting hydrogen sublattice. Experimentally at 160 GPa superconductivity transition temperature was measured to be 203 K [40], which is the first case for T_c above liquid nitrogen in hydrides. By two independent groups, LaH_{10} was synthesized, and its superconductivity transition temperature were reported 250 K at 170 GPa [41] and 260 K at 180-200 GPa [42], respectively. Interestingly, for such discovery, computational prediction using crystal structure searching play a critical role by guiding experimental synthesis [43, 44] and it becomes a reliable and essential tool for discovery of novel hydrides. For these systems, hydrogen sublattice are clearly formed and their arrays show monoatomic arrangement.

In 2020, room temperature superconductivity in carbonaceous sulfur hydride was reported [45]. In this experiment, a mixture of C-S-H reached ~ 270 GPa to obtain ~ 288 K, which is the highest T_c record up to now. Unlike other experimentally observed hydrides, crystal structure and stoichiometry are not determined yet and thus it is a still open question whether hydrogen forms its own metallic sublattice and what is the role of carbon and sulfur atoms. Considering high T_c in H_3S , we speculate that C-S-H compounds may have a similarity with H_3S and for example $[\text{H}_3\text{S}]^x[\text{C}]^{x+}$ might be possible, which can be understood as electron-doped H_3S .

Criticism of recent series of high T_c hydrides apparently exists. Computational crystal structure predictions and electronic structure calculations to estimate T_c quite well support experimental data and even guide synthesis. However, careful look of experimental data made us consider other scenarios because observed behaviors are not alike to other well-known superconductors and thus there is room for alternative interpretation. Hirsch and Marsiglio doubts high T_c superconductivity in hydrides and especially they pointed out an exceptional sharpness of the transition line with respect to temperature which is quite difference to other ones such as MgB_2 and YBCO [46].

Similar question was raised by Dogan and Cohen who suggested that whether C-S-H is a superconductor with anomalous behavior, or it undergoes metal-to-insulator(semimetal) transition induced by a structural phase transition [47].

3. Conclusion and perspectives

In the periodic table, hydrogen is grouped as alkali metals and Wigner-Huntington transition of molecular solid hydrogen is a way to realize it. However, the required hydrostatic pressure is still beyond our contemporary technique, and we circumvent the issue by utilizing chemical pressure in hydrides to reduce it significantly. With huge efforts from theory and experiments, these days we are witnessing high T_c superconductivity in hydrides at extremely high-pressure. While the transition pressure in hydrides is tractable, only several groups can reach such a high pressure, which play as a bottleneck of cross-check and reproducibility in this research field. Technical advancement in DAC can provide more accessibility to broader research groups. Moreover, it is natural to consider how to lower the transition pressure as a next step. Already multiple computational works report new ternary systems possessing high T_c at relatively low pressure. Ternary hydrides can be understood as doped metallic hydrogen sublattice in hydrides, which has potential to enhance superconductivity [48]. Confining hydrogen polymers with low dimensional geometry could be another route if we can make a clever design of substrates or channel environment [49]. Additionally, we can imagine a multi extreme conditions of static high-pressure and high irradiations. High irradiation condition is predicted to stabilize ionic hydrogen polymers and if one can generate multi extreme conditions with static high pressure, required external pressure for metallization may be further reduced in addition to chemical pressure effect.

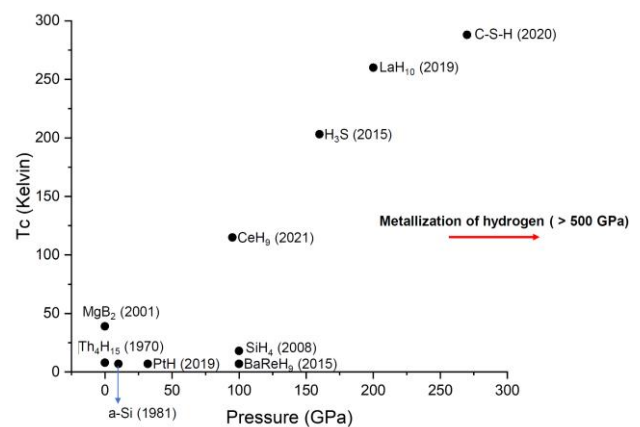


Fig. 2. A summary of experimentally reported superconducting hydrides under pressure discussed in the main text as well as a representative conventional superconductor (MgB_2). The discovered years are displayed next to the chemical formula in the parenthesis.

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