# Theory-directed discovery of high-temperature superconductivity in clathrate hydrides at high pressure

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The search for room-temperature superconductivity has been one of the great challenges in condensed matter physics ever since the first observation of superconductivity with a critical temperature ($T_c$) of 4 K in mercury in 1911. In recent years, we have been witness to the successful observation of superconductivity in highly compressed $SH_3$ ($T_c$ = 203 K at 155 GPa) and classes of clathrate hydrides (e.g., $CaH_6$, $YH_6$, $YH_9$, $LaH_{10}$), with $LaH_{10}$ holding a record high $T_c$ of 250–260 K at ~180 GPa among these binary hydrides (Figure 1).[1,2] Each of these experimental studies was guided by theoretical predictions. New experimental work on the Ca-H system has finally confirmed the theoretical calculation that launched this effort, the 2012 prediction of a high-$T_c$ superconductivity in $CaH_6$ above 200 K.[1–3]

First-principles structure-search methods, which require only the chemical composition as input without prior information about the arrangement of atoms, can identify the thermodynamically stable and metastable structures of materials at any pressure and 0 K. Armed with these state-of-the-art methods, several major materials discoveries under pressure have now been documented, one of which is the observation of an anti-Wilson transition:[4] the prototypical free-electron metal of sodium transforming to a transparent semiconductor at megabar pressures, in violation of the nearly 1-century old concept that the metallic state is the highest pressure form of materials. Subsequent structure-search simulations led to major discoveries of pressure-stabilized hydrides with $T_c$ approaching room temperature, realizing materials-by-design for this new class of materials.

In addition to the advanced structure-search methods, a key role in leading to the discovery of these high-$T_c$ superconducting materials is that the phonon-mediated Bardeen-Cooper-Schrieffer theory describes the high-$T_c$ superconducting properties of these hydrides remarkably well. According to this theory, high critical temperatures may be realized by a large density state at the Fermi level, a high average vibrational frequency, and strong electron-phonon coupling. In this regard, it has long been believed that atomic metallic hydrogen, which was first pointed out by Ashcroft in 1968, would be a very-high-$T_c$ superconductor, as it is predicted to exhibit the above electronic and vibrational properties.[1,2] However, the pressures required to produce atomic metallic hydrogen are estimated to become extremely high (~500 GPa), which creates a challenge for experimental characterization.

An alternative approach was later proposed by Ashcroft in 2004, in which hydrogen-rich materials may exhibit "chemical precompression" that could reduce the onset pressure of metallic hydrogen-like superconductivity by forming dense hydrides.[1,2] The structures of all high-$T_c$ hydrides studied to date can be viewed as various clathrate-like structures. From a Zintl-Klemm description, the metal atoms donate their valence electrons and weaken the $H_2$ molecules in these clathrate-like structures. Thus, the stability of these clathrate hydride

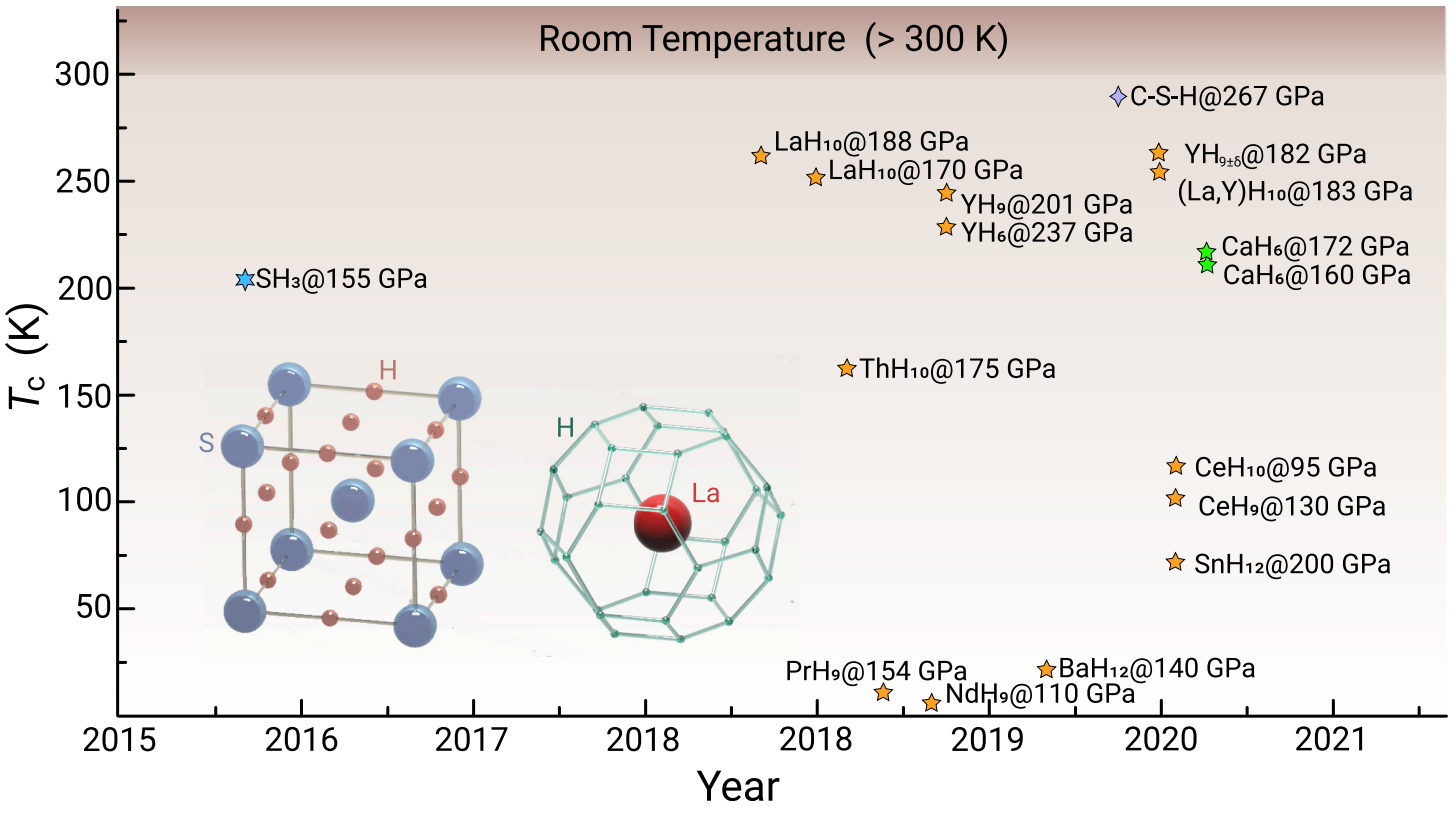


**Figure 1. Reported superconducting critical temperatures for various hydride superconductors since 2015**

structures can be considered to be a balance between the number of electrons available by charge transfer from the metal ions and the size of those metal ions. Electrons are shared to form connected networks of multi-center H … H … H bonds that resemble the bonding environment of atomic metallic hydrogen, and thus electronic properties such as high density of states at Fermi level, together with high characteristic vibrational frequencies and strong electron-phonon coupling.

The high superconductivity observed in compressed earth/actinide hydrides has ushered in a new era of superconductivity research, while this distinct type of clathrate metal hydrides was first proposed for $CaH_6$ using the crystal structure analysis by particle swarm optimization (CALYPSO) crystal structure prediction method in 2012.[3] Recent laser-heated diamond anvil cell experiments have confirmed this seminal prediction, with a $T_c$ of 215 K at ~170 GPa.[1] X-ray diffraction measurements are consistent with the predicted clathrate structure of $CaH_6$.[1] The results demonstrate that high $T_c$ above 200 K is indeed possible in clathrate hydrides formed from the main group, not only lanthanide/actinide, elements. These findings continue to demonstrate the role of structure search methods in this exciting new field.

In 2015, a variety of $T_c$ up to 203 K at ~155 GPa in sulfur hydrides was measured for the first time and exhibited high-$T_c$ above 200 K, thus sparking a flurry of interest in pressure-stabilized hydrides.[1,2] In this experiment, the initial sample of $SH_2$ has long been believed to dissociate into elemental hydrogen and sulfur at sufficiently high pressures. However, a theoretical study Led by Li and Ma in 2014 predicted two stable high-pressure structures, which were theoretically estimated to have the highest $T_c$ of 80 K at megabar pressure.[1,2] Stimulated by this excellent prediction, researchers synthesized two distinct high-temperature superconductors. One sample was prepared at low temperature and measured to exhibit $T_c$ from 30 to 150 K, in accordance with the predicted $SH_2$ superconductor. The other sample was annealed at room temperature and measured to have unexpected high-$T_c$ from 180 to 203 K, which was understood as the decomposition of $SH_2$ into high-$T_c$ $SH_3$ and S, where $SH_3$ is a known stoichiometry of $(SH_2)_2H_2$ that has been synthesized at a pressure of 7 GPa and was predicted to be a 200 K superconductor at megabar pressures.[1,2] This $SH_3$, as a matter of fact, was not molecular, and was also viewed as having a clathrate structure with S encapsulated in the cages of the hydrogen framework.[4] These excellent findings demonstrate that the theoretical work plays a critical role in the experiments into high-$T_c$ superconductors.

There is now a focus on broader chemical compositions, starting with ternary systems. A ternary phase consisting of carbon, sulfur, and hydrogen was reported to have a $T_c$ of 287 K at 267 GPa, but the composition and detailed structure at the highest critical temperature remain to be determined.[2] There is growing evidence that the introduction of even small amounts of a third element can enhance the superconductivity of binary hydrides through hole or electron doping as shown for the C-S-H and the La-N-H systems. A pressing task is also whether one can design a material with relatively high $T_c$ that is also stable at much lower pressures and even recoverable as a superconductor in ambient conditions. As shown in previous work, one of the key factors appears to spread favorable electron-phonon coupling over much of the vibrational spectrum in terms of these high-$T_c$ hydrides.[5] Beyond hydrides, other likely candidates are compounds consisting of other light elements such as Li, Be, B, and C, which ensure an essential ingredient that the system has a relatively high characteristic frequency. The recently predicted $LaBH_8$ and $LaBeH_8$ show intriguingly dynamic stability below 50 GPa, despite being thermodynamically stable at or above approximately 100 GPa.[2] These findings point to the potential of ternary hydrides as room temperature and "hot" superconductors under pressure as well as very-high-$T_c$ materials that are stable at low pressures. It is reasonable to expect that new classes of high-$T_c$ structures will be predicted and synthesized in the near future. To this end, recent advances in crystal structure prediction methods, data-driven machine learning techniques, and molecular dynamic simulations will undoubtedly accelerate the discovery of new and practical high-$T_c$ superconductors, as well as foster a deep understanding of physical phenomena, such as the possible coexistence of proton quantum dynamics together with hydrogen-induced superconductivity in very-high-$T_c$ hydrides.

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## DECLARATION OF INTERESTS

The authors declare no competing interests.