



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

Xin Zhong,¹ John S. Tse,^{1,2,*} Russell J. Hemley,^{3,*} and Hanyu Liu^{1,4,*}

¹International Center for Computational Method & Software and State Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun 130012, China

²Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon S7N 5E2, Canada

³Departments of Physics, Chemistry, and Earth and Environmental Sciences, University of Illinois Chicago, Chicago, IL 60607, USA

⁴International Center of Future Science, Jilin University, Changchun 130012, China

*Correspondence: john.tse@usask.ca (J.S.T.); rhemley@uic.edu (R.J.H.); hanyuliu@jlu.edu.cn (H.L.)

Received: February 10, 2022; Accepted: March 2, 2022; Published Online: March 29, 2022; <https://doi.org/10.1016/j.xinn.2022.100226>

© 2022 The Author(s). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Citation: Zhong X., Tse J.S., Hemley R.J., and Liu H. (2022). Theory-directed discovery of high-temperature superconductivity in clathrate hydrides at high pressure. *The Innovation* 3(2), 100226.

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

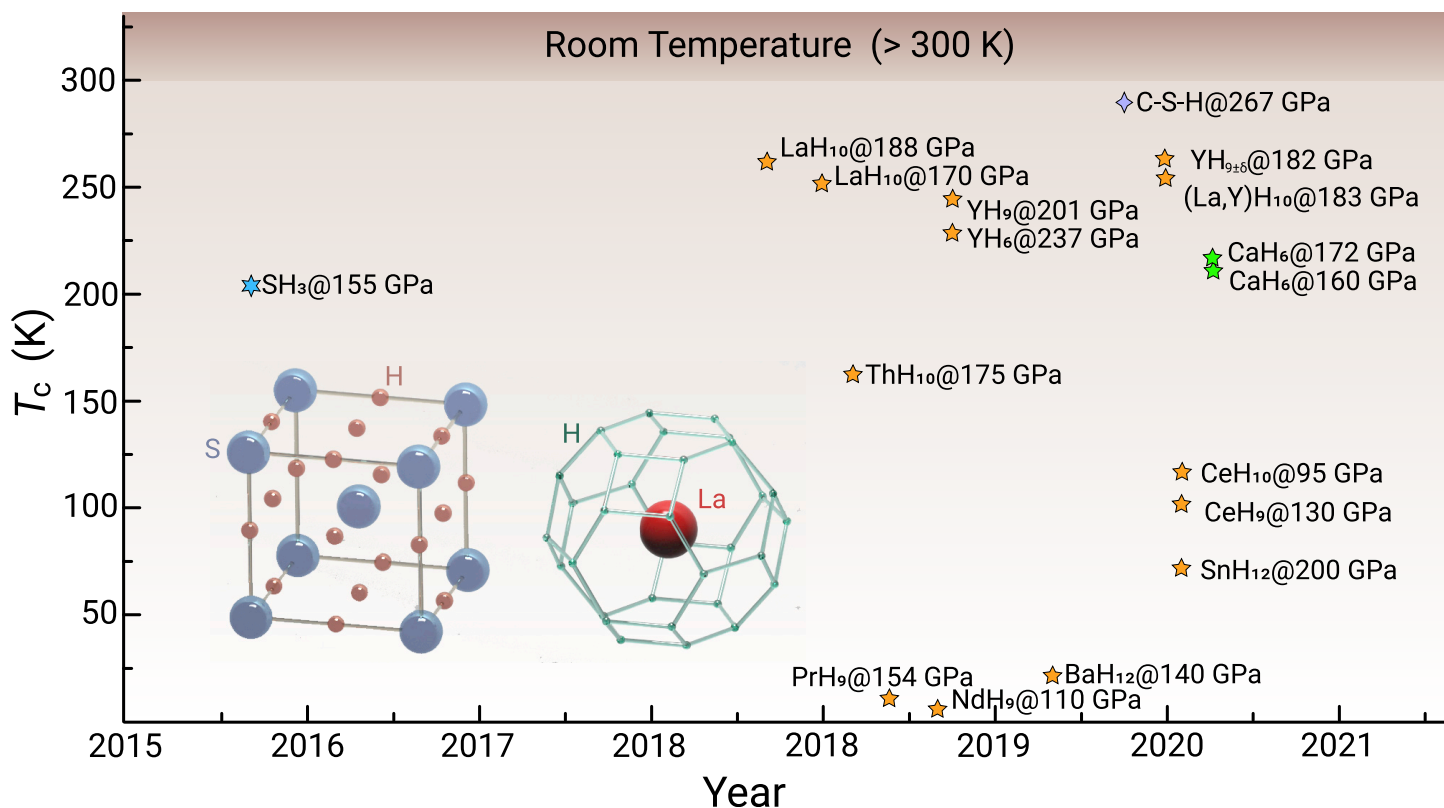


Figure 1. Reported superconducting critical temperatures for various hydride superconductors since 2015

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 $(\text{SH}_2)_2\text{H}_2$ 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.

REFERENCES

1. Gao, G., Wang, L., Li, M., et al. (2021). Superconducting binary hydrides: theoretical predictions and experimental progresses. *Mater. Today Phys.* **21**, 100546.
2. Hilleke, K.P., and Zurek, E. (2022). Tuning chemical precompression: theoretical design and crystal chemistry of novel hydrides in the quest for warm and light superconductivity at ambient pressures. *J. Appl. Phys.* **131**, 070901.
3. Wang, H., Tse, J.S., Tanaka, K., et al. (2012). Superconductive sodalite-like clathrate calcium hydride at high pressures. *Proc. Natl. Acad. Sci. U S A* **109**, 6463.
4. Ma, Y., Erements, M., Oganov, A.R., et al. (2009). Transparent dense sodium. *Nature* **458**, 182.
5. Tanaka, K., Tse, J.S., and Liu, H. (2017). Electron-phonon coupling mechanisms for hydrogen-rich metals at high pressure. *Phys. Rev. B* **96**, 100502(R).

ACKNOWLEDGMENTS

We thank Prof. Yanming Ma for valuable discussions. This work was supported by the National Key Research and Development Program of China (grant no. 2021YFA1400203), the National Natural Science Foundation of China (grant nos. 52090024, 12074138, and 11874176), the Fundamental Research Funds for the Central Universities (Jilin University [JLU]), the Program for JLU Science and Technology Innovative Research Team, and the Strategic Priority Research Program of Chinese Academy of Sciences (grant no. XDB33000000). R.J.H. acknowledges support from the U.S. National Science Foundation (grant no. DMR-210488). J.S.T. is supported by an NSERC Discovery Grant.

DECLARATION OF INTERESTS

The authors declare no competing interests.