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TOPICAL REVIEW — CALYPSO structure prediction methodology and its applications to materials discovery

The role of CALYPSO in the discovery of high-T_c hydrogen-rich superconductors*

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Hydrogen-rich compounds are promising candidates for high-T_c or even room-temperature superconductors. The search for high-T_c hydrides poses a major experimental challenge because there are many known hydrides and even more unknown hydrides with unusual stoichiometries under high pressure. The combination of crystal structure prediction and first-principles calculations has played an important role in the search for high-T_c hydrides, especially in guiding experimental synthesis. Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) is one of the most efficient methods for predicting stable or metastable structures from the chemical composition alone. This review summarizes the superconducting hydrides predicted using CALYPSO. We focus on two breakthroughs toward room-temperature superconductors initiated by CALYPSO: the prediction of high-T_c superconductivity in compressed hydrogen sulfide and lanthanum hydrides, both of which have been confirmed experimentally and have set new record T_c values. We also address the challenges and outlook in this field.

Keywords: CALYPSO, structure prediction, hydrogen-rich superconductors

PACS: 71.15.Mb, 74.25.Dw, 74.70.–b, 74.25.Jb **DOI:** 10.1088/1674-1056/ab4253

1. Introduction

Superconductivity, one of the most intriguing material properties, has sparked countless studies since its discovery in 1911.[1] Superconductors are categorized as either conventional (if their behaviour can be explained by the Bardeen–Cooper–Schrieffer (BCS) theory[2] or its derivatives) or unconventional (otherwise). Based on BCS theory, materials with light elements are especially favourable for achieving superconductivity because these elements provide high frequencies in the phonon spectrum. This theory has underpinned the design of conventional high-T_c superconductors. For many years, the development of superconductors was restricted by the Mcmillan limit,[3] which states that the maximum T_c in conventional superconductors cannot exceed 40 K. To overcome this limit, scientists addressed the following two questions. Are there conventional superconductors with T_c above 40 K in nature based on the known materials? What is the origin of the superconductivity? Ashcroft's proposal that solid hydrogen (H_2) and hydrogen-rich compounds represent candidates for high-T_c superconductors provided a turning point.[4,5] However, the metallization of solid hydrogen is challenging experimentally. A claim by Dias and Silvera to have observed atomic metallic hydrogen in the laboratory[6] remains controversial.[7,8]

Hydrogen-rich materials have become the main focus of superconductor research because metallization can be realized at lower pressures due to chemical precompression.[5] There are vast numbers of hydrides in nature, including many known hydrides and many new hydrides that can only be formed at high pressure. Therefore, discovering new hydrogen-containing superconductors by using traditional experimental methods based on trial and error is painstaking, and time-consuming work. Consequently, theoretical predictions are urgently required to guide the experimental synthesis of high-T_c superconductors. The key to designing H-containing superconductors at high pressure is to determine the crystal structures. Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO)[9–11] is one of the most efficient structure prediction methods, and only needs the

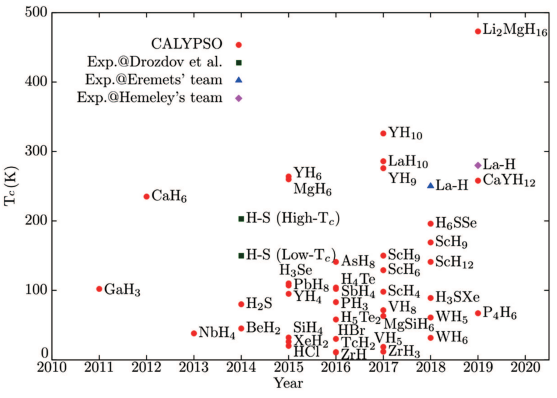


Fig. 1. Calculated and experimental T_c values of hydrogen-rich superconductors by year of publication. Solid red circles denote the calculated T_c of hydrogen-rich superconductors predicted by CALYPSO. Three experimental results are denoted by green squares, a blue triangle, and a pink diamond.

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chemical composition and external conditions, such as pressure, to predict stable and metastable structures in combination with first-principles calculations.[12–18] CALYPSO has theoretically predicted large numbers of superconductors,[19,20] some of which have been confirmed experimentally.

Given the accuracy and fruitful results of CALYPSO in searching for high-T_c superconductors, we present a review of the recent advances in the CALYPSO prediction of superconducting hydrides at high pressure (Fig. 1). Experimentalists have attempted to obtain many predicted superconductors, among which hydrogen sulfides[21] and LaH_{10}[22,23] have set record T_c values of 203 K and 250 K, respectively.

2. Superconductors predicted by CALYPSO

CALYPSO in combination with first-principles calculations has predicted many hydrides with high T_c values, including alkaline earth metal hydrides (e.g., CaH_6,[24] MgH_6[25]), rare-earth metal hydrides (e.g., YH_6,[26] YH_{10}, and LaH_{10}[27,28]), transition metal hydrides (e.g., NbH_4,[29] VH_8,[30] TcH_2,[31] WH_5, and WH_6[32]), boron group hydrides (e.g., GaH_3[33]), tetragen hydrides (e.g., SiH_4[34] and PbH_8[35]), pnictogen hydrides (e.g., PH_3,[36] P_4H_6,[37] and AsH_8[38]), chalcogen hydrides (e.g., H_2S,[39] H_4S_3,[40] H_3Se,[41] H_4Te, and H_5Te_2[42]), halogen hydrides (e.g., HBr[43] and HCl[44]), and noble gas hydrides (XeH_2[45]). These hydrides have a wide range of T_c values up to 326 K. The compressed hydrogen sulfides[39] and lanthanum hydrides[27,28] have been synthesized experimentally.[21–23] Thus, we discuss these two breakthrough compounds in detail.

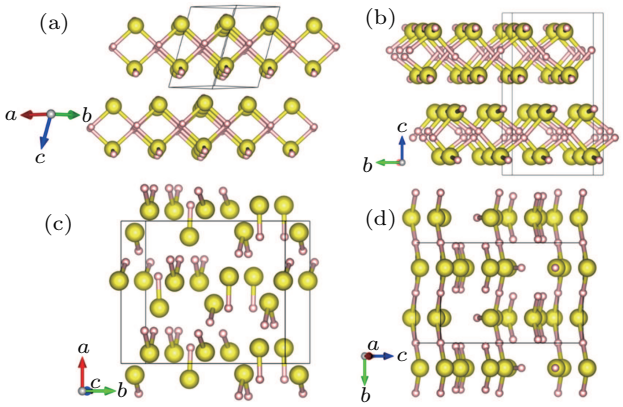


Fig. 2. Typical structures predicted by CALYPSO in sulfur hydrides: (a) $P\bar{1}$ H_2S (90 GPa), (b) *Cmca* H_2S (170 GPa), (d) $P2_12_12_1$ H_3S_4 (25 GPa), and (d) *Pnma* H_3S_4 (100 GPa). The small pink and large yellow spheres represent hydrogen and sulfur atoms, respectively.

2.1. Hydrogen sulphide: the first example of a predicted superconductor confirmed experimentally

As a typical molecular system, H_2S crystallizes in three different phases at ambient pressure.[46,47] Under high pressure, more complicated phases emerge theoretically and experimentally,[48,49] but these remain elusive.[39] H_2S was not initially identified as a promising superconductor because it was expected to dissociate into its constituent elements at high pressure (80 GPa) before metallization.[50,51] In 2014, CALYPSO predicted that H_2S is thermodynamically stable up to at least 200 GPa. In addition, the structure predictions also identified two metallic phases with space groups $P\bar{1}$ (Fig. 2(a)) and *Cmca* (Fig. 2(b)) that are stable above 80 GPa and are superconductor candidates with estimated T_c around 80 K.[39] Inspired by this prediction, Drozdov *et al.*[21] compressed the sulfur hydrides in a diamond anvil cell. They detected superconductivity by a sharp drop to zero resistance and magnetic susceptibility measurements. The measured T_c was sensitive to temperature, which suggested that there was a low-T_c phase with T_c of 33–150 K at 110–220 GPa when the samples were prepared at low temperature (< 100 K) and a high-T_c phase with T_c of 203 K when the sample was heated to room temperature. Drozdov *et al.* did not identify the two phases, however, they suggested that the low-T_c phase was H_2S because it agreed well with our predicted results.[39]

Many subsequent studies investigated the origin of the T_c value of 203 K. Theoretical studies reported that the high-T_c phase originated from H_3S, formed by the decomposition of compressed H_2S at high pressure.[52–58] H_3S was first synthesized in 2011 by Strobel *et al.*, and then was predicted as a superconductor with a high T_c of ~ 200 K,[50] close to the experimentally observed high T_c value.[21] The decomposition product of compressed H_2S was studied under high pressure by first-principles structure predictions and x-ray diffraction (XRD) experiments.[40] In addition to H_2S and H_3S, CALYPSO predicted new stoichiometries of H_2S_3, H_3S_2, HS_2, and H_4S_3. Based on these results, a possible dissociation path for H_2S of $8H_2S \rightarrow S + 4H_3S + H_4S_3$ was proposed and confirmed by high-pressure XRD experiment. This was also the first demonstration of the partial decomposition of H_2S into H_3S at high pressure. The co-existence of H_3S and H_2S provided direct evidence that explained the experimental observation of two superconductive phases. The $P2_12_12_1$ and *Pnma* structures of H_4S_3 are shown in Figs. 2(c) and 2(d), respectively, and the *Pnma* phase is superconducting with T_c of ~ 2 K at 140 GPa.

The mechanism of the superconductivity at 203 K in compressed hydrogen sulfide at high pressure has been widely studied to aid the design of new high-T_c superconductors.[52,58–60] Several theoretical studies revealed that covalent bonding plays a key role in the large electron–phonon coupling.[61–63] To establish the relationship between T_c and covalent bond strength, we constructed a hypothetical compound, H_6SSe, by substituting half of the S atoms in H_3S with Se atoms.[62] Using the unbiased CALYPSO method, we identified three dynamically stable structures (Figs. 3(b)–3(d)). These three structures retain the main $Im\bar{3}m$ cubic framework of H_3S (Fig. 3(a)) with different Se substitution

positions, leading to the formation of covalent S–H and Se–H bonds with different bond strengths. To investigate the effect of covalent bonding on the high T_c of chalcogen hydrides, we plotted T_c as a function of bond strength reflected by the Laplacian $\nabla^2\rho$ (Fig. 3(e)). T_c decreased from 195 to 115 K as the strength of the weakest covalent H–S or H–Se bond in each structure decreased, indicating that strong covalent bonds are important in determining the high T_c of the H_3S system.

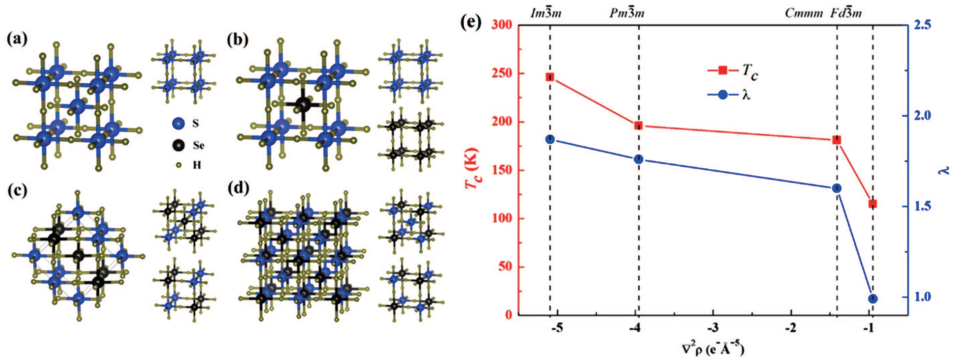


Fig. 3. (a) $Im\bar{3}m$ structure of H_3S and the predicted (b) $Pm\bar{3}m$, (c) $Cmmm$, and (d) $Fd\bar{3}m$ structures of H_6SSe at 200 GPa. (e) T_χ and electron–phonon coupling constant λ as functions of bond strength of the weakest covalent bonds in H_3S and H_6SSe.

2.2. Clathrate hydrides: a leap to room-temperature superconductivity

2.2.1. LaH_{10}

Hydrogen sulfide superconductivity is not the only prediction that has been confirmed experimentally.[21] In 2017, two separate CALYPSO studies of lanthanum hydride systems revealed new compounds with stoichiometries of LaH_3, LaH_4, LaH_5, LaH_8, and LaH_{10}, as well as the known compound LaH_2.[27,28] LaH_{10} was predicted to be dynamically stable above 220 GPa with a face-centred cubic (fcc) structure (space group $Fm\bar{3}m$) that was a unique H_{32} clathrate-like structure, consisting of four H squares and 12 H hexagons (Fig. 4(a)). The T_c of LaH_{10} was estimated to be 257–274 K at 250 GPa, which is close to room temperature. The astonishing predicted T_c in LaH_{10} prompted these hydrides to be experimentally synthesized. Just after the theoretical work was published, Geballe *et al.*[64] synthesized the lanthanum superhydrides $LaH_{10\pm x}$ ($-2 \leq x \leq 1$) by directly compressing La and H_2 samples at 170 GPa and 1000 K. They subsequently published a different synthesis route using ammonia borane (NH_3BH_3) as the hydrogen source,[22] which produced $LaH_{10\pm x}$ at pressures of 180–200 GPa. They observed sharp drops in resistivity when they cooled the samples to 260 K, which indicates the superconducting transition. Drozdov *et al.*[23] also reported the superconductivity of fcc LaH_{10} with T_c of 250 K at 170 GPa, synthesized by direct reaction of lanthanum and hydrogen under high pressures. The superconductivity was supported by the observation of zero resistance, the isotope effect, and a decrease in T_c upon the application of an external magnetic field. Previously, they had reported a T_c of 215 K in lanthanum hydrides,[65] which may correspond to other LaH_x phases. The measured T_c of 250–260 K from the two independent experiments agree well with the predicted T_c of LaH_{10},[27,28] which demonstrates that CALYPSO is a powerful tool in the search for high-T_c superconductors.

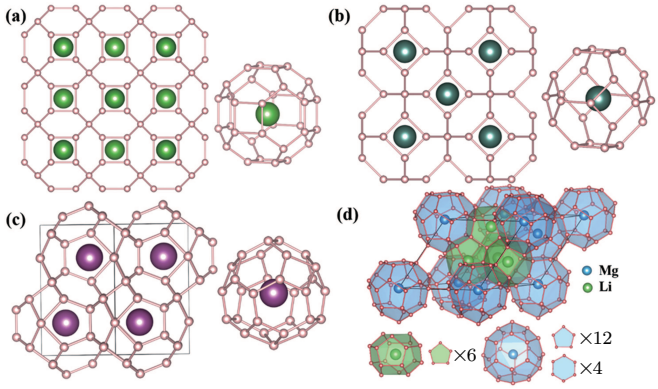


Fig. 4. Clathrate hydrides predicted by CALYPSO. (a) $Fm\bar{3}m$ La(y)H_{10}, (b) $Im\bar{3}m$ Ca(y)H_6, (c) $P6_3/mmc$ Sc(Y, Ce)H_9, and (d) $Fm\bar{3}m$ Li_2MgH_{16}.[66] The building block metal atoms centred in the H_{32}, H_{24}, H_{29}, H_{18} and H_{28} cages are also shown in each panel.

2.2.2. Other clathrate hydrides

LaH_{10} was not the first structure containing an H-cage to be predicted. In 2012, Ma's group used CALYPSO to predict that a new calcium hydride, CaH_6, could be synthesized by compressing elemental calcium and hydrogen or CaH_2 and hydrogen.[24] In the CaH_6 structure, hydrogen atoms linked by weak covalent bonds form a clathrate with a calcium atom at the centre (Fig. 4(b)). This unique body-centred cubic structure had a predicted T_c of 235 K at 150 GPa, which was the first time that a T_c of more than 200 K was predicted for a hydride. Later, this type of structure was also found in yttrium hydrides. In 2015, using CALYPSO, we predicted that a yttrium atom can react with six hydrogen atoms to form YH_6 at 120 GPa with the same structure as CaH_6 and a higher T_c of 264 K,[26] approaching room temperature. In 2017, in the same study that predicted LaH_{10}, YH_{10} was predicted to have a T_c of up to 305–326 K at 250 GPa, surpassing room temperature.[27,28]

Ref. [28] also found that H atoms could form different cages in the rare earth (RE = Sc, Y, La, Ce, Pr, etc.) hydrides, such as, H_{24} in REH_6, H_{29} in REH_9, and H_{32} in REH_{10} (Fig. 4). Surprisingly, it is also demonstrated that the calculated T_c for the clathrates increases with increasing H cage size. For example, YH_6, YH_9, and YH_{10} have T_c of 264 K (120 GPa), 276 K (150 GPa), and 303 K (400 GPa), respectively. Other RE hydrides, LaH_9, CeH_9, CeH_{10}, and PrH_9, had much lower T_c (< 56 K) due to the higher mass of the RE elements, although ScH_6 and ScH_9 had T_c of ~ 190 K. Liang *et al.* used CALYPSO to predict the ternary clathrate hydride, $CaYH_{12}$,[67] which had a similar H clathrate structure to YH_6 and CaH_6 and possessed a T_c of 258 K at 200 GPa. More recently, Ma's group predicted a clathrate structure in ternary hydride, Li_2MgH_{16}[66] with space group $Fm\bar{3}m$ (Fig. 4(d)), which contains Li-centered H_{18} cages and Mg-centered H_{28} cages. In particular, it exhibits a T_c of around 473 K at 250 GPa, the highest T_c in all the hydrides, which provides the possibility to obtain superconductivity even higher than room temperature.

3. Other superconductors

Owing to the high-T_c superconductivity of hydrogen sulfide, hydrides of elements neighbouring S, such as P,[36,38,68,69] Se,[41] and Te,[42] have been investigated.

3.1. Phosphorus hydrides

Just after the experimental observation of superconductivity in compressed H_2S, Drozdov *et al.* compressed PH_3,[70] an analogue of H_2S, and observed a high T_c of ~ 100 K around 200 GPa, indicated by the abrupt drop to zero resistance. However, they did not identify the origin of the superconducting phase. Analogous to the decomposition of hydrogen sulfides, PH_3 may also decompose to new P–H compounds. Hence, it is important to search for new structures and stoichiometries to explain the origin of the T_c of ~ 100 K. CALYPSO structure prediction has been vital in exploring the origin of the superconductivity in phosphorous hydrides. In 2016, Liu *et al.* performed a structure search in the PH_x ($x = 1, 2, 3, 4, 5$) system at high pressure with CALYPSO.[36] The $P2_12_12_1$ (< 210 GPa, Fig. 5(a)) and $C2/m$ (> 210 GPa, Fig. 5(b)) phases of PH_3 were discovered at high pressure. The calculated T_c of the $C2/m$ phase was 83 K, which agreed well with the experimental results. However, these two phases were predicted to be energetically unstable, and decomposed into P and H at high pressure.

Wang's group explored the decomposition of PH_3 at high pressure via a combination of experiments and CALYPSO prediction.[37] XRD and Raman measurements showed that PH_3 underwent decomposition at high pressures to produce a new stable compound, P_4H_6. P_4H_6 is generated stepwise. First, dimerized PH_3 decomposes to P_2H_4: $2PH_3 \rightarrow P_2H_4 + H_2$. Then, P_4H_6 is generated by the further decomposition of P_2H_4: $2P_2H_4 \rightarrow P_4H_4 + H_2$. At low temperatures, P_4H_6 can be observed up to 200 GPa.[70] However, the exact structure could not be determined experimentally. CALYPSO predicted the metallic structures of P_4H_6 to be $Cmcm$ (< 182 GPa, Fig. 5(c)) and $C2/m$ (> 182 GPa, Fig. 5(d)). In addition, the T_c of the $C2/m$ phase was estimated to be 67 K at 200 GPa, which agreed with the measured T_c, indicating that P_4H_6 could be the superconductor observed experimentally by Drozdov *et al.*[70]

3.2. Other chalcogen hydrides

In 2016, Ma's group used CALYPSO to predict three metallic stoichiometries of HSe_2, HSe, and H_3Se, all of which exhibit superconductivity.[41] H_3Se had the same cubic structure ($Im\bar{3}m$) (Fig. 3(a)) as H_3S and had a predicted T_c of 110 K at 250 GPa. Although H_3Se and H_3S have the same structures, the spectral functional are different because the Se atoms are heavier, which contributes to the lower T_c. In the same year, they identified three metallic stoichiometries of H_4Te, H_5Te_2, and HTe_3. Unlike the covalent bonds of H–S(Se) in $H_3S(Se)$, the H–Te bonds in tellurium hydrides are ionic bonds.[42] Especially, $P6/mmm$ H_4Te (Fig. 6(a)) contains elongated "H_2" molecules, which is a superconductor with estimated T_c of 104 K at 170 GPa. While H_5Te_2, with space group $C2/m$ (Fig. 6(b)), has a relatively lower T_c of 58 K at 200 GPa.

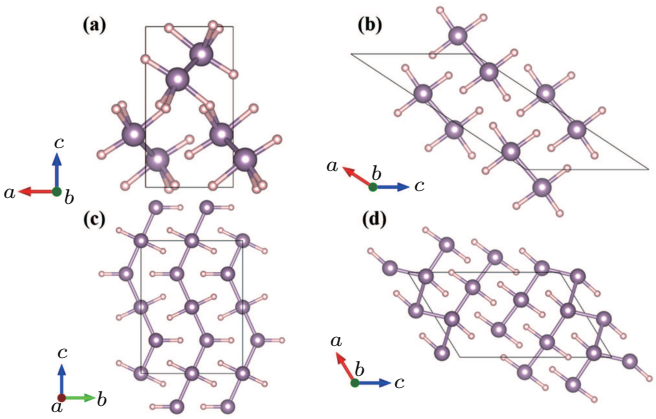


Fig. 5. Structures of phosphorus hydride compounds predicted by CALYPSO. (a) $P2_12_12_1$ PH_3, (b) $C2/m$ PH_3, (c) $Cmcm$ P_4H_6, and (d) $C2/m$ P_4H_6.

3.3. Other hydrides

In addition to the typical hydride superconductors, CALYPSO has predicted other hydrogen-containing superconductors (Fig. 1) such as GaH_3,[33] NbH_4,[29] BeH_2,[71] PbH_8,[35] SiH_4,[34] HCl,[44] HBr,[43,44] AsH_8,[38] SbH_4,[38] TcH_2,[31] Zr–H,[72] Sc–H,[73] Xe–H,[45] V–H,[30] H_3SXe,[74] W–H,[32] and $MgSiH_6$.[75] However, their T_c values are low

(10–140 K). Thus, we do not discuss them in detail in this review.

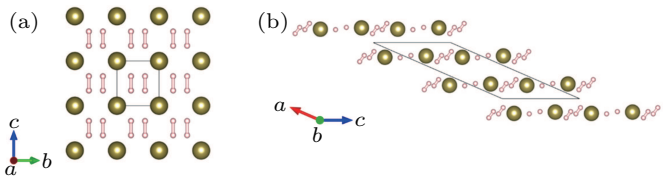


Fig. 6. Structures of tellurium hydrides predicted by CALYPSO. (a) $P6/mmm$ H_4Te and (b) $C2/m$ H_5Te_2.

4. Summary and outlook

We have summarized progress in high-T_c superconductors predicted by CALYPSO, and described the prediction of H_2S and LaH_{10}, which stimulated subsequent experimental studies. The observed T_c values of these compounds of 250–260 K pave the way to room-temperature superconductivity. Crystal structure prediction has been important in finding high-T_c superconductors. Because theorists have calculated T_c of binary hydrides for most elements in the periodic table, research can now focus on ternary hydrides as the next area in which to discover superconductors, however, the computational burden for these studies will be far higher. Experimentalists still face the challenge of synthesizing theoretically predicted materials. Furthermore, reducing the pressures at which superconducting phases appear is also a major challenge, so that superconductivity can be observed outside of diamond anvil cells and used in practical applications. The search for superconductors with higher T_c is another area of research. For example, predicting clathrate structures with larger cages may be a possible route to higher-T_c superconductors.

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