Usage Report for Fiscal Year 2021

Project Title:

Crystal Structure Prediction and High-temperature Superconductivity of Li-RE-H System at Pressures

Name:

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1. Background and purpose of the project, relationship of the project with other projects

Clathrate superhydride is a class of hydrides in which metal atoms act as guests in hydrogen (H) cages, while H atoms are weakly covalently bonded with each other and the H–H distance of approximately 1.0 Å is close to that (0.98 Å) in atomic hydrogen at 500 GPa. The first-ever sodalite-like clathrate superhydride CaH_6 is predicted to have high T_c values of 220–235 K at 150 GPa, which has been recently successfully synthesized by two independent experiments. Inspired by the prediction of CaH_6, other compressed clathrate superhydrides, such as LaH_{10} and YH_{10}, are predicted to have higher T_c values at high pressure, approaching room-temperature superconductivity. Encouraged by these predictions, subsequent experiments synthesized a variety of Rare-Earth (RE) clathrate superhydrides, of which the measured T_c of YH_6, YH_9, and LaH_{10} reach high values at 220, 243, and 250-260 K, respectively, setting a new record of T_c = 260 K in known superconductors. The high superconductivity of these clathrate superhydrides arises from H atoms because the H electrons contribute substantially to the electron density of states at the Fermi level ($N(E_f)$). These excellent theoretical and experimental effort indicates the hydrogen clathrate framework plays an important role in improving superconductivity, thereby implying clathrate superhydrides are the most promising candidates for room-temperature superconductivity.

Theoretically predicting more hydrides with a hydrogen clathrate framework would help expand the number of potential candidates for high-temperature superconductors. As the number of elements increases, the number of conceivable structures and possible superconducting compounds in complex hydrides grows rapidly, suggesting there might be more high-temperature superconductors in ternary hydrides than in binary hydrides. There have been many theoretical and experimental studies on ternary superconducting superhydride at high pressure, including several clathrate structured materials, such as a $LaBH_8$ composition was predicted exhibits T_c of 126 K at 50 GPa, $CaYH_{12}$ have calculated T_c values of 230–258 K at 180–200 GPa, and cubic hexahydride $(La,Y)H_6$ with measured T_c of ~237 K and decahydrides $(La,Y)H_{10}$ with a measured T_c of ~253 K have been synthesized at 183 GPa. Recently, through the strategy of introducing extra electrons via metal doping into known H_2-rich binary systems, we have already identified a metastable “hot” superconductor of Li_2MgH_{16} with a theoretical T_c value well above room temperature (T_c = 473 K at 250 GPa). However, this interesting Li_2MgH_{16} phase exhibits a metastable feature, then the search for thermodynamically stable ternary clathrate superhydrides with high T_c values thus remains a key issue in the research field of high-temperature superconductivity.

In an attempt to seek ternary stable clathrate superhydrides that have even higher H content than

Li_2MgH_{16}, the H lattices of ternary hydrides should involve more electrons from the metal elements than that in Li_2MgH_{16}. It is noteworthy that Rare-Earth (RE) elements have more valence electrons than Mg, and RE elements such as Y can provide more electrons due to their small electronegativities, enabling the donation of more electrons to the H lattice. This indicates that high-temperature superconducting clathrate superhydrides may be expected in Li-RE-H compounds.

Here we report an extensive exploration of the high-pressure phase diagrams of Li-RE-H (RE = Sc, Y, La) compounds. In this work, by focusing on H-rich species with performing structure searches, we identified several thermodynamically stable and high-temperature superconducting ternary compounds. Among these predicted stable structures, Fd3m structured Li_2YH_{17} and Li_2LaH_{17} are clathrate superhydrides with predicted T_c values up to 112 and 156 K, respectively.

2. Specific usage status of the system and calculation method

During the fiscal year 2021, 1.8 million CPU hours were used to investigated hydrides with high superconductivity in this project. We employ our developed swarm-intelligence-based CALYPSO structure prediction method, which is designed to search for the stable structures of given compounds, for the investigation of phase stability of Li-RE-H compounds at 300 GPa. For most cases, the structure search for each chemical composition converges (evidenced by a lack of any additional structure with lower energy) after 1000 ~ 1200 structures were investigated. The energetic stability of different ternary stoichiometries is evaluated by their formation enthalpy of dissociated into the most competing element and binary compounds. The underlying energetic calculations are performed with the plane-wave pseudopotential method as implemented in the VASP code. The Perdew-Burke-Ernzerhof generalized gradient approximation is chosen for the exchange-correlation functional. The electron-ion interaction is described by projector-augmented-wave potentials with 1, 3, 11, 11, and 11 valence electrons for H, Li, Sc, Y, and La atoms, respectively. Kinetic cutoff energy of 700 eV and Monkhorst-Pack k meshes with a grid spacing of 0.25 $Å^{-1}$ are adopted to ensure the enthalpy converges to better than 1 meV/atom. The phonon spectrum and electron-phonon coupling (EPC) of the stable compounds are calculated within the framework of linear response theory through the Quantum-ESPRESSO code, where ultrasoft pseudopotentials were used with a kinetic energy cutoff for wavefunctions of 60 Ry and a kinetic energy cutoff for charge density and potential of 750 Ry. 3 ×3 ×3 q-meshes and 12 ×12 ×12 k-meshes were used for stable Li–RE–H ternaries to compute the EPC matrix elements. Electron-phonon couplings (EPC) constant λ, ω_{log}, and T_c are solved using the elk code, as derived by the direct solution of the isotropic MigdalEliashberg equation.

3. Result

YH_{24} is the most H-rich binary rare-earth hydride, containing 12 H_2 molecules per formula unit. To mimic the behavior of introducing extra electrons via Li doping into 1–2 f.u. binary rare-earth superhydrides, we examine the phase diagram of $Li_xRE_yH_z$ (RE = Sc, Y, and La. x = 1–3, y = 1–2, z = 10–48) at 300 GPa, as shown in FIG. 1, where we focused on H-rich species. $LiScH_{10}$, Li_2ScH_{20}, Li_2YH_{17}, $Li_3Y_2H_{36}$, and Li_2LaH_{17} are found to become stable at 300 GPa. Metastable compounds and unstable compounds with formation enthalpy values lower than 100 meV/atom are also shown, represented with blue and red squares, respectively. In previous high-throughput material discovery studies, it is noteworthy that the convention structure searches for the threshold between metastable (likely to be

synthesized) or unstable (unlikely to be synthesized) compounds are 50 meV/atom.

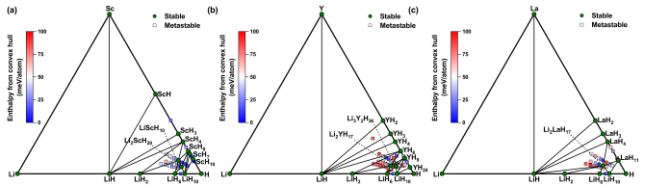

Fig 1. Calculated phase diagram of (a) Li-Sc-H, (b) Li-Y-H, and (c)Li-La-H compounds at 300 GPa, respectively. Blue and red squares denote metastable or unstable phases with different formation enthalpies. Green circles indicate thermally stable phases. Black lines between green circles connect stable phases.

In this work, the five newly predicted thermally stable ternary Li-RE-H compounds are all highly symmetric at 300 GPa: space group of LiScH10, Li_2ScH_{20}, Li_2YH_{17}, $Li_3Y_2H_{36}$, and Li_2LaH_{17} is R-3m, Immm, Fd-3m, C2/m, and Fd-3m, respectively (as shown in FIG. 2). We found that both the $LiScH_{10}$ and Li_2ScH_{20} consist of strongly covalently bonded H_2 molecular units and weakly covalently bonded atomic hydrogen layers. These two phases also can be referred to as $LiSc(H_2)_2H_6$ and $Li_2Sc(H_2)_4H_{12}$, respectively. Remarkably, Li_2YH_{17} and Li_2LaH_{17} consist of H_{20} and H_{28} cages, where Li and Y or La are in the center of hydrogen cages. $Li_3Y_2H_{36}$ consists of H_{20} cages, where Li atoms or H_2 molecules are in the center of H_{20} cages. In other words, this structure can be regarded as Li_2YH_{17} after replacing a quarter of Li atoms with H_2 molecules and then can be referred to as $[(H_2)Li_3]Y_2H_{34}$. The symmetry of $Li_3Y_2H_{36}$ is much lower than that of Li_2YH_{17}, which is attributed to the symmetry breaking caused by the H_2 molecule units. Lattice dynamics analysis of Li-RE-H compounds indicated that R-3m–$LiScH_{10}$, Immm–Li_2ScH_{20}, Fd-3m–Li_2YH_{17}, and Fd-3m–Li_2LaH_{17} can be dynamically stable at pressures down to 150, 250, 150, and 160 GPa, respectively.

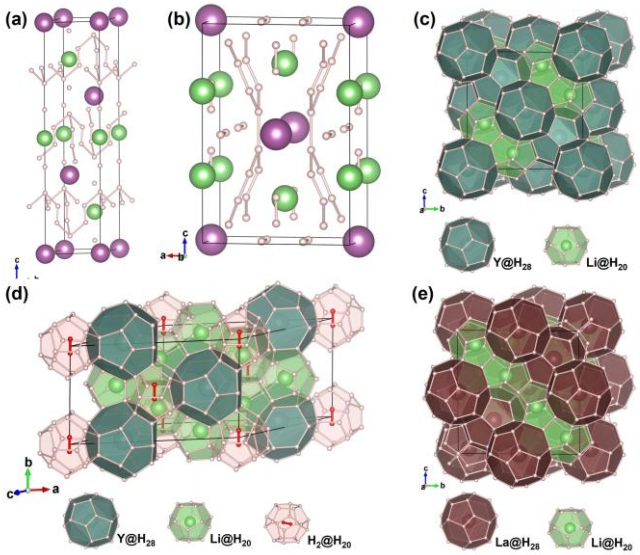

Fig 1. Conventional cells of (a) R-3m–$LiScH_{10}$, (b) Immm–Li_2ScH_{20}, (c) Fd-3m–Li_2YH_{17}, (d) C2/m–$Li_3Y_2H_{36}$, (e)Fd-3m–Li_2LaH_{17} at 300 GPa. The light green, purple, dark green, and brown spheres represent Li, Sc, Y, and La metal atoms, respectively. Both red and pink spheres are Hatoms, and different colors are used to characterize bonding characteristics between H atoms. Fd-3m–Li_2YH_{17}, C2/m–$Li_3Y_2H_{36}$, and Fd-3m–Li_2LaH_{17} are all clathrate structures, consisting of Li-centered H_{20}, H_2-centered H20, Y-centered H_{28}, and La-centered H_{28} cage units. All the hydrogen cage units are presented using translucent polyhedrons.

All the predicted thermodynamically stable Li-RE-H ternaries are metallic at 300 GPa, as confirmed by the electronic density of states calculations (see FIG. 3). Similar to other clathrate superhydrides (such as CaH_6, YH_9, LaH_{10}, and Li_2MgH_{16}), clathrate structured Li-RE-H compounds possess high H-dominated electronic density of states values at the Fermi level ($N(E_f)$). Li-Sc-H compounds, consisting of H_2 molecular unit and atomic hydrogen layers, also have large $N(E_f)$ values, where $N(E_f)$ of Li_2ScH_{20} is also H-dominated due to the high H content and atomic hydrogen layers.

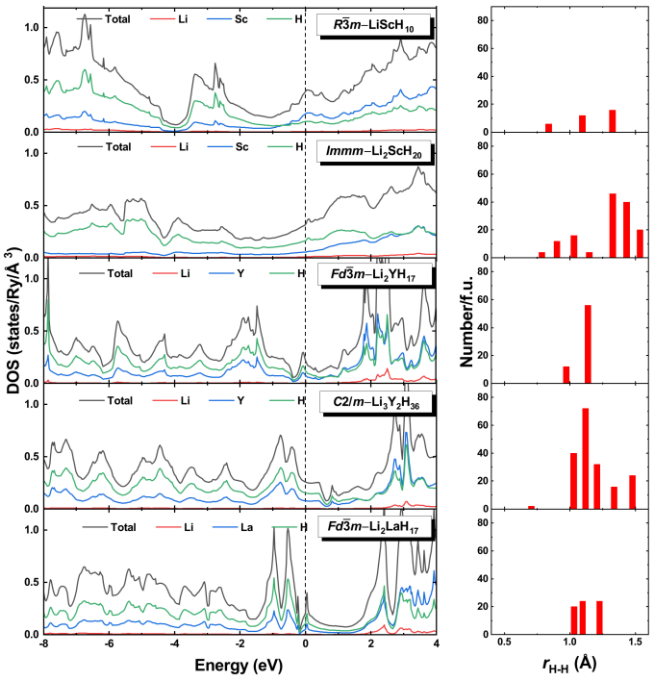

Fig 2. Projected density of states (left panel) and histogram of H–H distances (right panel) for stable Li–RE–H compounds at 300 GPa.

Hydrides that possess high H-dominated N(E_f) are usually high-temperature superconducting materials, so electron-phonon coupling properties of thermodynamically stable Li-RE-H ternaries were studied (as shown in Table I and FIG. 4). Using the ELK code, T_c values were estimated by numerically solving the isotropic Migdal-Eliashberg equation. Numerically solving the Migdal-Eliashberg equation can help to obtain the superconducting energy gap values versus temperature. The maximum value of temperature corresponding to the superconducting energy gap is not zero defines the T_c value. When the Coulomb shielding pseudopotential μ^* is set to be 0.10, T_c of R-3m–LiScH$_{10}$, Immm–Li$_2$ScH$_{20}$, Fd-3m–Li$_2$YH$_{17}$, and Fd-3m–Li$_2$LaH$_{17}$ is estimated to be up to 75 K at 150 GPa, 242 K at 300 GPa, 108 K at 200 GPa, and 156 K at 160 GPa, respectively, and the corresponding electron-phonon coupling constant are 0.90, 1.81, 0.99 and 1.80, respectively. Although neither Li$_2$YH$_{17}$ nor Li$_2$LaH$_{17}$ are potential room-temperature superconductors, they are thermodynamically stable clathrate structural prototypes. It is noteworthy that wholly or partially replacing Li/Y/La atoms with other metal atoms or small molecules could help to hunt more classes of high-temperature superconducting clathrate superhydrides.

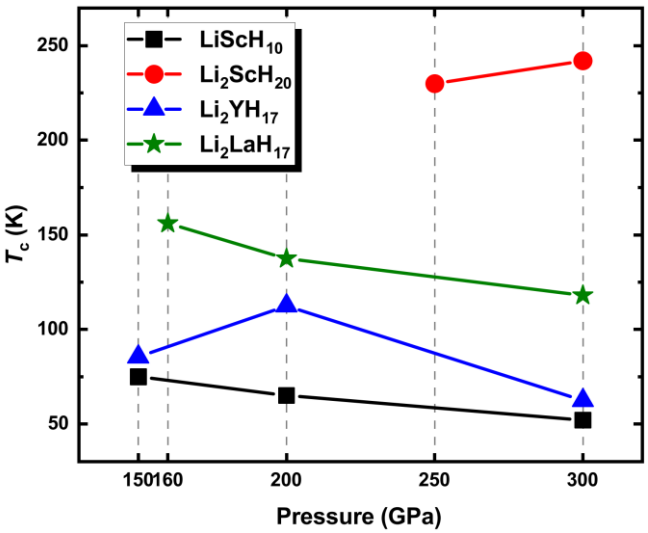

Fig 4. The superconducting transition temperatures of R-3m–LiScH$_{10}$, Immm–Li$_2$ScH$_{20}$, Fd-3m–Li$_2$YH$_{17}$, and Fd-3m–Li$_2$LaH$_{17}$ at different pressures.

Table I. N(E_f) (states/Ry/f.u.), λ, ω_{log} (K), and T_c (K) values estimated using μ^*=0.10(0.13) for R-3m–LiScH$_{10}$, Immm–Li$_2$ScH$_{20}$, Fd-3m–Li$_2$YH$_{17}$, and Fd-3m–Li$_2$LaH$_{17}$ at different pressures (GPa).

Compound	Pressure	$N(E_f)$	λ	ω_{log}	T_c
$R\bar{3}m$–LiScH$_{10}$	300	2.48	0.67	1538	52(40)
	200	2.75	0.78	1351	65(53)
	150	2.95	0.90	1161	75(65)
$Immm$–Li$_2$ScH$_{20}$	300	7.55	1.81	1404	242(223)
	250	7.46	1.86	1294	230(211)
Fd-3m–Li$_2$YH$_{17}$	300	5.98	0.69	1758	64(50)
	200	6.06	0.99	1332	108(93)
	150	6.38	0.85	1390	83(69)
Fd-3m–Li$_2$LaH$_{17}$	300	9.73	0.86	1854	118(99)
	200	9.16	1.14	1324	138(123)
	160	9.11	1.80	1274	156(142)

4. Conclusion

In summary, by searching the high-pressure phase diagram of the Li-RE-H system using the CALYPSO crystal structure prediction method and software, several thermodynamically stable superhydrides

were proposed to be high-temperature superconductors. T_c values of clathrate structured Fd-3m–Li_2YH_{17} and Fd-3m–Li_2LaH_{17} are estimated to be up to 108 and 156 K at 200 and 160 GPa, respectively. Besides, a superhydride, Immm–Li_2ScH_{20}, composed of H_2 molecular unit and the atomic hydrogen layers, is predicted to be a high-temperature superconductor with the highest T_c value of 242 K at 300 GPa. Clathrate structured Li_2YH_{17} and Li_2LaH_{17} could be used as a prototype structure, and superconductivity might be improved by replacing Li and Y/La with other metal elements. Our results indicate ternary compounds are promising candidates for exploring high-temperature superconductivity under high pressure.

5. Schedule and prospect for the future

I have been a HOKUSAI general user and wish to continue using the system. During the last fiscal year 2021, I have finished work on Li-RE-H compounds, and am preparing the manuscript for publication in the journal of Physical Review Letters. For the next fiscal year, we plan to continue using the HOKUSAI supercomputer to study the stability and superconductivity of clathrate structures based on clathrate structured Li_2MgH_{16}, Li_2YH_{17}, and $LaBH_8$. By changing metal elements, new high-temperature superconductors, and even room-temperature superconductors are expected to be proposed. We expect high-standard publications can be eventually achieved.

Fiscal Year 2021 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

Potential Room Temperature Superconductivity in Clathrate Lanthanide/Actinides Octadechydrides at Extreme Pressures, DOI: 10.21203/rs.3.rs-1148583/v1, 2021
Xin Zhong, Ying Sun, Toshiaki Iitaka, Meiling Xu, Hanyu Liu, Changfeng Chen, Yanming Ma

Crystal Structures and Superconductivity of Carbonaceous Sulfur Hydrides at Pressures up to 300 GPa, Physical Review B, under review, 2022
Ying Sun, Xue Li, Toshiaki Iitaka, Hanyu Liu, and Yu Xie