Usage Report for Fiscal Year 2020

Project Title:

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

Name:
Yanming MA (1), Ryotaro ARITA (1), ○Toshiaki IITAKA (2)
Laboratory at RIKEN:
(1) RIKEN Center for Emergent Matter Science, First-Principles Materials Science Research Team,
(2) RIKEN Center for Computational Science, Discrete Event Simulation Research Team

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

Theoretically design hydrogen-rich ternary hydrides with high superconducting critical temperature (T_c) has attracted great attention, which can provide a guidance for experimental synthesis. In our previous studies, we are successful to design a range of binary superconducting hydrides (e.g., CaH_6, YH_6, YH_9, and LaH_{10} *etc.*) with high T_c values above 200 K by using CALYPSO code. Encouragingly, most of those predicted hydrides have been synthesized in the subsequent experiment (e.g., experimental T_c values for YH_6 and YH_9 are 220 and 240 K, respectively). Remarkably, the theory-orientated finding of the LaH_{10} superconductor creates a high Tc value in the range of 250-260 K, a record high T_c among known superconductors.

Binary hydrides have been exhaustedly investigated by either simulations or experiments. LaH_{10} remains as the best superconducting example up to date. To search further for a high temperature superconductor, ternary or quaternary superhydrides are promising candidates as we have already demonstrated by designing a ternary clathrate Li_2MgH_{16} superconductor that can be regarded as a "hot" superconductor with a theoretical T_c value reaching 470 K at 250 GPa. Recent experiment did measure a high T_c value at 288 K in the C–S–H system though composition and structure information are missing. As the number of elements increases the number of conceivable superconducting structures grows rapidly, bringing ternary superhydrides to be better hunting ground for high temperature superconductors.

Here we systemically explored the high-pressure crystal structures of Li-RE-H (RE = Sc, Y, La) system through our CALYPSO method on crystal structure prediction for more high-temperature superconductors. The coordination environments, chemical bonds, crystal structure, electronic properties, and superconductivities of Li-RE-H at various pressures were studied. Our results proposed the *Fd*-3*m* phase of Li_2YH_{17}, where the H-sublattice in this structure adopted the same framework type MTN in the database of zeolite structures, to be a new high temperature superconductors clathrate hydride, with T_c values up to 112 K under high pressure.

2. Specific usage status of the system and calculation method

During the fiscal year 2020, 7.2 million CPU hours were used to investigated hdyrides with high superconductivity in this project. Universal variable–composition structure searches for $Li_xRE_yH_z$ (RE = Sc, Y, and La. $x = 1 \sim 3$, $y = 1 \sim 2$, $z = 1 \sim 32$) were performed with CALYPSO structure prediction method, which requires only chemical compositions for a given compounds to predict stable or metastable structures at given pressure, using simulation cells that consists of maximal number of 50 atoms. Fixed-composition structural predictions were conducted to ensure the calculation reach the

convergence. 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 total energy calculations and local structural relaxations were carried out using the density functional theory as implemented in the VASP code. To estimate the superconducting transition temperature (T_c), we calculated the electron-phonon coupling properties using the Quantum ESPRESSO code.

3. Result

We have performed variable-composition structure searches in ternary hydrides $Li_xRE_yH_z$ (RE = Sc, Y, and La. x = 1 ~ 3, y = 1 ~ 2, z = 1 ~ 32) over a wide range of hydrogen contents at high pressures. While there isn't any stable ternary hydride predicted for Sc, various thermodynamically stable superhydirdes have been identified for Y and La at 300 GPa, such as Li_2YH_{17}, $Li_3Y_2H_{36}$, $LiLaH_{10}$, and Li_2LaH_{14}, as indicated by the convex hull shown in Fig. 1,.

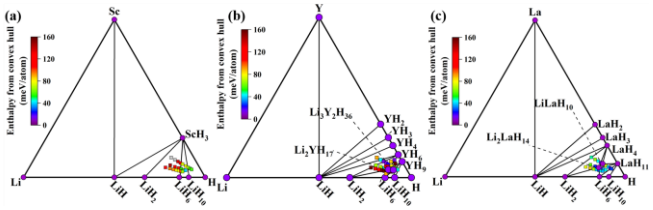

Fig 1. Calculated phase diagram of (a) Li-Sc-H, (b) Li-Y-H, and (c)Li-La-H compounds at 300 GPa, respectively. Colored squares denote metastable phases with different formation enthalpies. Purple circles indicate thermodynamically stable phases.

Among these four superhydrides, only Li_2YH_{17} and $Li_3Y_2H_{36}$ adapt clathrate structure, with space groups of *Fd*-3*m* and *P*1, respectively. In order to compare and analyze the similarities and differences of the structures between these two clathrates, Fig. 2 shows the structures of the primitive cell of the two clathrates from a similar angle. It is found that both hydrogen clathrates are composed of H_{20} and H_{28} cages. The *Fd*-3*m* phase Li_2YH_{17} consists of H_{20} cages centered on Li atoms and H_{28} cages centered on Y atoms; *P*1 phase $Li_3Y_2H_{36}$ consists of H_{20} cages centered on Li atoms or H_2 molecules and H_{28} centered also on Y atoms. The *P*1 phase $Li_3Y_2H_{36}$ can be regarded as H_2 molecules partially replacing the Li atoms in the *Fd*-3*m* phase Li_2YH_{17}. Therefore, the *P*1 phase $Li_3Y_2H_{36}$ can also be referred to as Li_2YH_{17} and simply referred to as $[H_2Li_3]Y_2H_{34}$. The symmetry of $Li_3Y_2H_{36}$ is much lower than that of Li_2YH_{17}, or it stems from the symmetry breaking caused by the H_2 molecular unit.

It is worthy noting that, as shown in Fig. 3, the hydrogen cage network in the *Fd*-3*m* phase Li_2YH_{17} is the same as the MTN zeolite network. This similarity is not uncommon in hydrogen clathrates. LaH_{10}, ThH_{10}, and YH_6, which are theoretically predicted but confirmed by subsequent high-pressure experiments. Their hydrogen cage networks are the same as AST, AST, and SOD zeolite networks, respectively. There is no imaginary frequency to be found in phonon dispersion of the *Fd*-3*m*-Li_2YH_{17} at 140 GPa, indicating dynamically stability of this predict structure at low pressures.

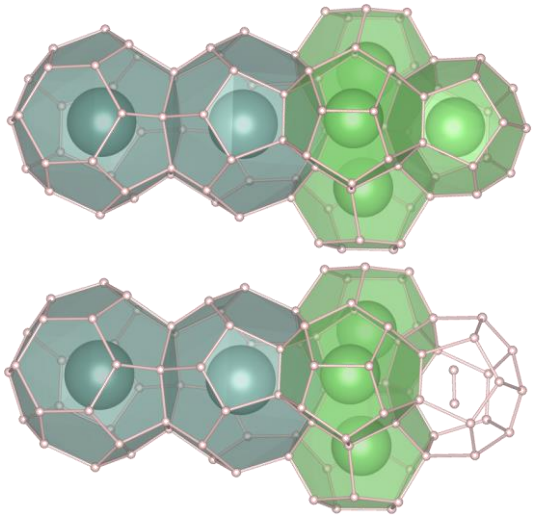

Fig 2. The crystal structure of primitive cell of *Fd*-3*m* phase Li_2YH_{17} (top) and *P*1 phase $Li_3Y_2H_{36}$ (bottom) at 300 GPa. The large and small balls represent Li/Y and H atoms, respectively, and the light green and dark green balls represent Li and Y atoms in the center of the H cage, respectively.

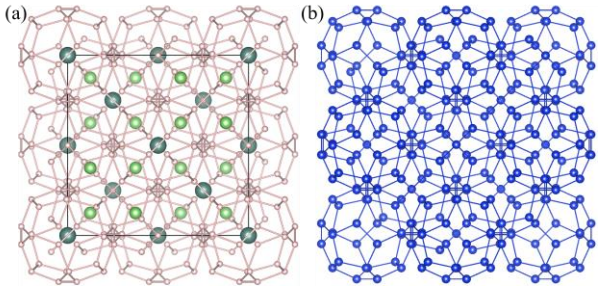

Fig 3. (a) The unit cell structure of *Fd*-3*m* phase Li_2YH_{17} and (b) the MTN type framework in the zeolite structure database. Light pink, light green, dark green and dark blue spheres represent H, Li, Y and Si atoms, respectively.

Bader charge analysis was performed to explore the charge transfer between atoms of the predicted hydrogen-rich Li-Y-H compounds. The results reveal that electron transfers from Li and Y atoms to H atoms, which indicates that Li and Y atoms are both positively charged electron donors, while H atoms are negatively charged electron acceptors.

Furthermore, we have calculated the electron-phonon coupling parameters of *Fd*-3*m* Li_2YH_{17}. By using the ELK code to numerically solve the standard Allen-Dynes modified McMillan equation and Migdal-Éliashberg equation, the superconducting transition temperature T_c of cubic phase Li_2YH_{17} at different pressures is estimated, as shown in Table 1. Numerically solving the Migdal-Éliashberg equation can obtain the superconducting energy gap Δ versus temperature *T*. When the Coulomb shielding pseudopotential μ^* is set to 0.10, the superconducting critial temperature of *Fd*-3*m* cubic phase Li_2YH_{17} is estimated to be 32, 85, 112, and 62 K at 140, 150, 200, and 300 GPa, respectively, where the corresponding electron-phonon coupling parameters are 0.58, 0.85, 1.00 and 0.66, respectively. The electro-acoustic coupling strength and superconducting transition temperature of Li_2YH_{17} first increase and then decrease upon compression. The estimated maximum T_c of predicted Li_2YH_{17} is 112 K at 200 GPa, as shown in Table 1.

Table 1. The superconductivity of *Fd*-3*m* phase Li_2YH_{17} under high pressures.

Pressure (GPa)	λ	ω_{log} (K)	T_c (K), Éliashberg	
			$\mu^* = 0.10$	$\mu^* = 0.13$
140	0.58	1396	32.3	23.1
150	0.85	1390	85.4	71.6
200	1.00	1284	112.5	95.7
300	0.66	1806	62.3	48.1

For *P*1 phase $Li_3Y_2H_{36}$, it can be viewed as the substitution product of the H_2 molecule partly replacing the Li atoms in the *Fd*-3*m* phase Li_2YH_{17}. However, the presence of H_2 molecules breaks the symmetry, resulting in a much lower symmetry than Li_2YH_{17}, implying the superconducting temperature *P*1 phase $Li_3Y_2H_{36}$ might be lower than that of *Fd*-3*m* Li_2YH_{17}.

4. Conclusion

In summary, we have performed extensive structure searches on Li-RE-H system through CALYPSO crystal structure prediction method. We found two thermodynamically stable clathrate compounds Li_2YH_{17} and $Li_3Y_2H_{36}$ at 300 GPa, where the H-sublattice in these structures adopts the same framework type MTN in the database of zeolite structures. The further electron-phonon coupling calculations indicate the highest estimated T_c of Li_2YH_{17} could reach 112 K at 200 GPa. Our results suggest the structure of Li_2YH_{17} might be used as prototype structure to design clathrate superhydrides by replacing Li and Y with other metal atoms or small molecules and clusters.

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 2020, I have finished work on Li-RE-H

compounds, and am preparing the manuscript for publication in the journal of Physical Review B. For the next fiscal year, we plan to continue using the HOKUSAI supercomputer to study the stability and superconductivity of structures based on Li_2MgH_{16} and Li_2YH_{17}. By replacing Li, Mg, and Y atoms with other 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.

6. If no job was executed, specify the reason.

Fiscal Year 2020 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

Computational Discovery of Dynamically Stable Cubic SH3-like High-Temperature Superconductor at 100 GPa via CH4 Intercalation, Phys. Rev. B 101, 174102 (2020).

Ying Sun, Yifan Tian, Bowen Jiang, Xue Li, Hefei Li, Toshiaki Iitaka, Xin Zhong, and Yu Xie