

Project Title:

Prediction of Crystal Structure and Properties

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

Solid hydrogen was predicted to become metallic under very strong compression and will probably become an high-temperature superconductor. However, hydrogen remains insulating up to extremely high pressures, at least up to 342 GPa, at both low- and room- temperatures. It is assumed that metalization is more accessible for hydrogen-rich compounds, since hydrogen can be "pre-compressed" by the heavier elements. Indeed, subsequent experiments showed that AlH_3 transforms to a metal-hydrogen alloy at a pressure in excess of 100 GPa, which was significantly lower than that required to metalize pure hydrogen itself. Recently, extended M-H (M=Li, Na, K, Rb and Cs) systems have received much attention. Several hydrogen-rich compounds, for instance LiH_6 , NaH_9 and CsH_3 , were proposed to form at moderate pressures. Moreover, our theoretical studies on Ca-H system suggested that stoichiometric CaH_6 with hydrogen that forms sodalite cages containing enclathrated Ca stabilizes at 150 GPa and possesses a strong electron-phonon coupling with an estimated superconducting temperature in the order of 200 K.

The current research project aims to explore the high pressure crystal structures on hydrogen rich hydrides of MH_n , (M=Be, Mg, and Ba, $n \geq 2$) through our CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) method on crystal structure prediction, thus zero temperature high pressure phase diagram can be established. We then wish to perform extensive electron-phonon coupling calculations using the predicted high pressure metallic structures within the linear response theory

to understand if these compounds can be superconducting at high pressures.

The ultimate goal of the current research is then targeting to reveal the possibility of high temperature superconductivity on these hydrides under ultra-high pressure and to understand the exciting chemistry of hydrogen and the role played on the superconductivity, guiding the future experimental exploration on high temperature superconductivity at high pressures. We expect the current research project could establish important underlying physics on the superconductivity of hydrogen-rich compounds and also lead us high standard publications in top journals, such as Physical Review Letters or PNAS.

2. Specific usage status of the system and calculation method

During the fiscal year 2012, We have used all of the total allocated CPU time of CPU hours for above calculations.

Ab initio crystal structure prediction has been performed through our newly developed particle swarm optimization technique, which has been implemented in our CALYPSO code. This method is able to search for the structure possessing the lowest free energy at given Pressure-Temperature conditions and is capable of predicting the stable structure of a given compound for a given composition. The structural relaxations were performed with the VASP code. We use plane wave basis sets for the expansion of the electronic wave function, a pseudopotential description of the electron-ion interactions and density function theory

(DFT) for the electron-electron interactions through Quantum-ESPRESSO packages. It can calculate the ground-state energy and Kohn-Sham orbitals for both insulators and metal, in any crystal structure, for different exchange-correlation functions. The calculation of the phonon dispersion curves is performed within the direct supercell method via Phonopy package or the linear response theory based on the DFT via Quantum-ESPRESSO.

3. Results

We have explored the structures of BeH_{2n} , MgH_{2n} , BaH_{2n} , and SrH_{2n} ($n = 1 - 6$) hydrides. For each stoichiometry, calculations were performed at pressures 50-300 GPa with up to four formula units in the model. The enthalpies of candidate structures relative to the products of dissociation into $\text{MH}_2 + \text{solid H}_2$ at the appropriate pressures are calculated. Fig.1 summarized the most interesting results on SrH_{2n} . The essential information can be summarized as follows: (i) stable structures began to emerge at pressures < 50 GPa; (ii) SrH_4 was the most stable phase at pressures between 50, while at 100 GPa SrH_6 had the lowest enthalpy of formation; (iii) the breakup of hydrogen molecules depended on the Sr/H ratio, and a higher susceptibility to dissociation was observed at higher ratios. Notably, calcium hydrides with stoichiometry having odd number of hydrogen (e.g. SrH_3 , SrH_5 , and SrH_7 , etc) were found to be energetically very unfavourable and were excluded in the discussions.

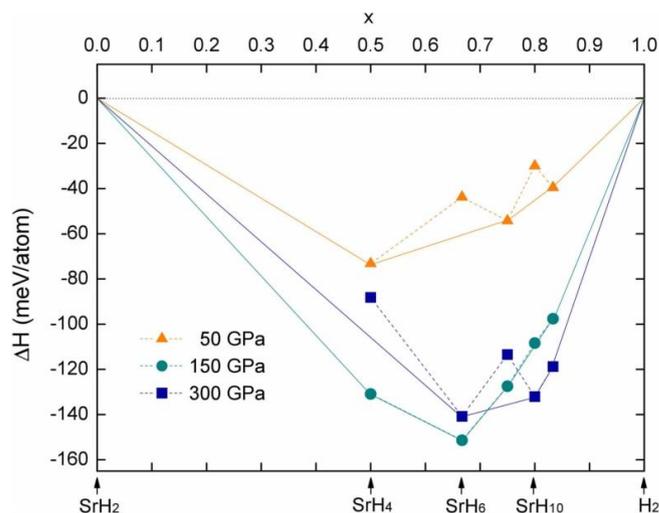


Figure 1 | Enthalpies of formation (ΔH , with respect to SrH_2 and H_2) of SrH_{2n} ($n=2-6$) and crystal structures. The abscissa x is the fraction of H_2 in the structures. The stable pressure ranges for SrH_4 and SrH_6 are 50 GPa and 100–200 GPa, respectively.

At 50 GPa, SrH_4 adopts the $cI10\text{-CaH}_4$ structure, in which hydrogen forms monatomic $\text{H} + \text{H}_2$. The band structure calculation reveals that SrH_4 is an insulator. At 100 GPa, the P-6 structure becomes energetically most stable, and SrH_6 becomes the most stable stoichiometry of SrH_{2n} ($n=1-6$). Three hexagonal phases of SrH_6 having P-6, P321 and R-3m structures were predicted to be stable at pressures of 100 to 300 GPa. As shown in Fig. 2, Sr adopts the same atomic sites in all three structures and H locates in the interstitial region. Three types of hydrogen species, monatomic $\text{H} + \text{H}_2$, “ H_3 ” units and trispiral H chain, were observed. The P-3 structure has a primitive hexagonal structure including $6\text{H}_2 + 6\text{H}$. The next stable phase has a P321 structure, which can be seen as an intermediate phase on the way of hydrogen transforms from monatomic $\text{H} + \text{H}_2$ to trispiral H chain in the R-3m structure.

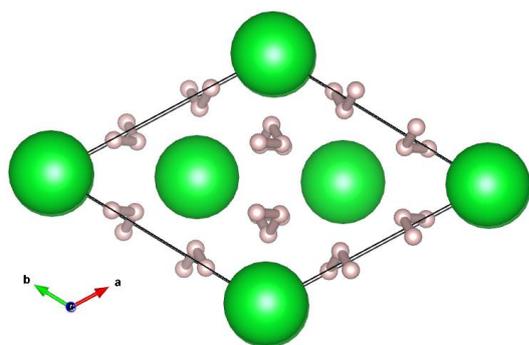


Figure 2 | Crystal structure of R-3m SrH₆

Recently, several novel hydrogen species, e.g. “H+H₂”, “H₃” and “H₄” units, have been predicted in hydrogen-rich materials, e.g. Li-H, Cs-H, and Ca-H systems, which have been shown to bring several intriguing properties in hydrides at high pressures, such as, dynamical Jahn-Teller effect, phonon anomalous, and strong electron-phonon coupling. Therefore, the electronic, phonon and electron-phonon coupling properties of the novel trispiral H chains in SrH₆ is very interesting.

The electronic properties of the three hexagonal phases of SrH₆ were systematically investigated by density of state (DOS), band structure, electron localization function and Bader charge analysis calculations. As shown in Fig. 3, the metallization of SrH₆ by band gap closure has been found at 150 GPa in P-3 structure. The partial DOS of hydrogen at the Fermi level increases from ~0 to ~0.1 electrons per SrH₆ as the pressure increases from 150 to 200 GPa and remain constant to 300 GPa, which are comparable to that of cI14 CaH₆ at 150 GPa, indicating the P321 structure a potential high-temperature superconductor.

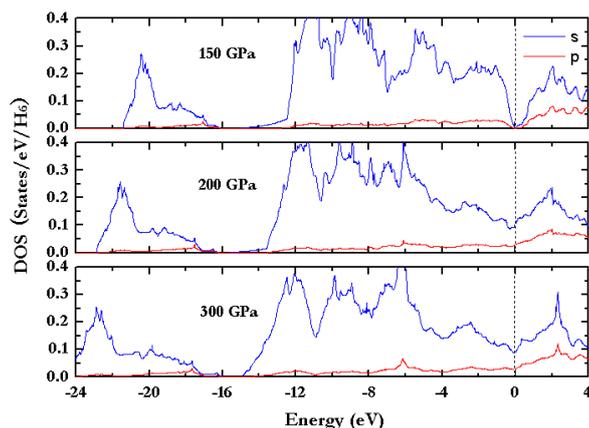


Figure 3 | Partial DOS of hydrogen in SrH₆. P-3 structure

at 150 GPa, P321 structure at 200 GPa and R-3m structure at 300 GPa.

In the phonon calculations, we found several imaginary frequencies for all the three, P-3, P321 and R-3m structures of SrH₆ outside the energetically stable range of pressures. One soft mode of P-3 structure was found in Γ -H direction at 200 GPa, and a detailed analysis of the vibration eigenvector of this soft mode reveals that the P-3 \rightarrow P321 is a displacive phase transition of second order. Besides, we found that the P321 structure transform to the R-3m structure during the structure optimization at pressures in range of 250 to 300 GPa, and one soft mode in L- Γ direction was also found for R-3m structure at 250 GPa, which indicate P321 \rightarrow R-3m is also a displacive phase transition.

The predicted stable structures for BeH₂ were carefully optimized at a higher level of accuracy at pressure range from 0 to 300 GPa for enthalpy curve calculations. Our simulations revealed a sequence of new structures under pressure. Among them, a simple hexagonal P-3m1 structure shows the lowest enthalpy at 50 GPa as depicted in Fig. 4(b) (1 f.u./cell), It presents an obvious layered structure with six-fold H-Be-H sandwiches stacking order seeing in the polyhedral views (3 formula units/unit cell, f.u./cell). The tilt BeH₆ octahedrons connected to each other vertically to form a layer with an average 1.42 Å of Be-H distance. With increasing pressure, a similar hexagonal R-3m structure has taken place at 141 GPa, which is built up by the similar sandwich-like layers with different stacking sequences (ABC-ABC). This pressure induced phase transition caused a slight distortion on the position of the center Be atoms along the [100] crystallographic direction. The nearest H-H distance in R-3m is 1.43 Å at 150 GPa, which is much longer than the H-H bonding length of ~1.2 Å and decreases very slowly with increasing pressure and become 1.39 Å at 300 GPa, showing that H atoms do not present any bonding trend. In the contrast of these two six-coordinated BeH₂, the experimental phase

α -BeH₂ is a structure consists of corner sharing BeH₄ tetrahedra unit. Interestingly, when it is further squeezed to the pressure of 202 GPa, a three dimensional framework of orthorhombic structure with Be centered in an eight-fold structure formed by BeH₈ hendecahedrons consisting of two-face capped trigonal prisms was predicted (4 formula units/unit cell, f.u./cell).

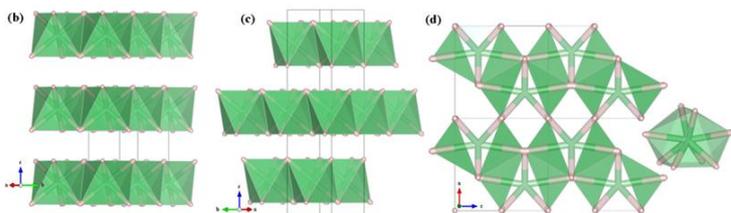


Fig. 4 | The predicted $P-3m1$ (b), $R-3m$ (c), and $Cmcm$ (d) structures.

The calculated enthalpy curves (relative to α -BeH₂) for various structures at zero temperature (presented in Fig. 5) confirm the energetic stability of our predicted structures. It is clearly seen that our $P-3m1$ phase exhibits a more preferred thermodynamic stability than that of the previously predicted β -BeH₂ structure, which is never stable in all pressures studied. And this $P-3m1$ structure is stable up to 141 GPa, above which the $R-3m$ structure becomes favorable and stable in the pressure range of 141 – 202 GPa. At higher pressures (> 202 GPa), the $Cmcm$ phase becomes the most stable structure. Not that, at 0 K, Gibbs free energy (G) reduces to enthalpy + zero-point energy (ZPE). Beryllium and hydrogen have very light atomic mass, and thus its ZPE may be large enough to affect the structural stabilities. To investigate the ZPE effects of BeH₂, we have thus calculated G_s of $P-3m1$, $R-3m$ and $Cmcm$ structures at 100-250 GPa using quasi-harmonic approximate; see inset of Fig. 5. It turns out that inclusion of ZPE lowers the stabilization pressures of $R-3m$ and $Cmcm$ structures, while the existence of our newly predicted structures remains unchanged.

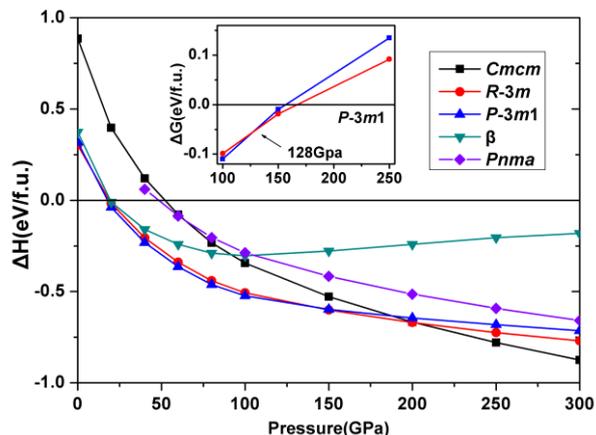


Fig. 5 | Calculated enthalpies (relative to α -BeH₂) of various structures as function of pressure in BeH₂. Inset shows calculated Gibbs free energies for the $P-3m1$ and $R-3m$ structures with the zero-point corrections.

4. Conclusion

The phase diagram of BeH_{2n}, MgH_{2n}, BaH_{2n}, and SrH_{2n} ($n = 1 - 6$) hydrides at zero temperature were established. Especially, we found that the results for SrH_{2n} and BeH_n ($n=1-6$) at 0 K are quite interesting, worthy of publication in high profile journals. We found the most stable stoichiometry for Sr hydrides are SrH₄ and SrH₆ at pressure of 50 GPa and above 100 GPa, respectively. An unexpected hydrogen species of trispiral H chain has been predicted in the $R-3m$ structure of SrH₆ at pressure of 300 GPa. Electronic structure calculations suggest that the $P321$ and $R-3m$ structures of SrH₆ are potential high-temperature superconductors at pressures above 200 GPa. Besides, we found that both $P-3 \rightarrow P321$ and $P321 \rightarrow R-3m$ are displacive phase transitions of the second order.

Three new phases were found for BeH₂ under high pressure. $P-3m1$ structure is found to be stable up to ~130 GPa, at which pressure we predict a phase transition into another insulating structure with $R-3m$ symmetry. Further increasing pressure, above ~200 GPa, this $R-3m$ phase undergoes a structural transition from a semiconductor phase to a metallic phase with symmetry $Cmcm$. Moreover, the estimated T_c of BeH₂ reach 45 K at 300 GPa by

application of the Allen-Dynes modified McMillan equation.

5. Schedule and prospect for the future

We have been a RICC general user and wish to continue using the system. During the fiscal year 2012, We have performed systemically structure predictions, electronic band structures, phonons, electron-phonon calculations on BeH_{2n} , MgH_{2n} , BaH_{2n} , and SrH_{2n} ($n = 1 - 6$) hydrides. But only part of the planed calculations on BaH_{2n} has been finished. For example, most of structural predictions on BaH_{2n} ($n= 1-6$) were done. But the calculations on electronic band structures, electron localization function, electron-phonon couplings were not completely finished yet. For the next fiscal year 2013, we plan to continue using RICC supercomputer to perform the rest of calculations on BaH_n , then we will extend our research on the crystal structure prediction of other systems through CALYPSO code, and build the zero pressure phase diagram. We expect high standard publications can be eventually achieved.

Fiscal Year 2012 List of Publications Resulting from the Use of RICC

[Publication]

1. Hui Wang, **John S. Tse**, Kaori Tanaka, **Toshiaki Iitaka**, and **Yanming Ma**, "Superconductive "sodalite"-like clathrate calcium hydride at high pressures", **Proc. Natl. Acad. Sci. USA** **109**, 6463 (2012).
<http://dx.doi.org/10.1073/pnas.1118168109>
2. Hui Wang, **John S. Tse**, **Toshiaki Iitaka**, and **Yanming Ma**, "Superconductive Sr hydride at high pressures", (in preparation, 2013).
3. Ziwei Wang, Li Zhu, Hanyu Liu, Hui Wang, **Toshiaki Iitaka**, and **Yanming Ma***, Metallization and Superconducting of BeH₂ Under High Pressure, (in preparation, 2013).
4. **Zhi Li**, Robert Laskowski, **Toshiaki Iitaka**, Takami Tohyama, "First-principles calculation of helical spin order in iron perovskite SrFeO₃ and BaFeO₃", Phys. Rev. B 85, 134419 (2012).
<http://link.aps.org/doi/10.1103/PhysRevB.85.134419>
5. **Zhi Li**, **Toshiaki Iitaka**, and Takami Tohyama, "Pressure-induced ferromagnetism in cubic perovskite SrFeO₃ and BaFeO₃", Phys. Rev. B 86, 094422 (2012) .
<http://link.aps.org/doi/10.1103/PhysRevB.86.094422>