

Project Title:

**High pressure structures and superconductivity of hydrogen-rich compounds
(CaH_n and SrH_n, n=4-8)**

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1. Background and purpose of the project

Solid hydrogen was predicted to become metallic under very strong compression and will probably become an extraordinary high-temperature superconductor, because of its high Debye temperature due to the lightest atomic mass. However, hydrogen remains insulating up to extremely high pressures, at least up to 342 GPa. Recently, N. W. Aschroft has proposed that the mainly covalent metallic hydrides of methane, silane, germane, and stannane could be the high temperature superconductors under high pressure when they are metallic. Indeed, the previously theoretical calculations on silane, germane, and stannane have revealed very high superconducting transition temperatures (T_c) of 55 K at 125 GPa, 64 K at 220 GPa, 52-62 K at 200 GPa.

The current research project aims to explore the high pressure crystal structures on hydrogen rich alkaline earth hydrides of CaH_n, MgH_n, SrH_n, and BaH_n through our newly developed particle swarm optimization technique (PSO) on crystal structure prediction, thus zero temperature high pressure phase diagram can be established. Then it is necessary to find the high pressure metallic structures of these hydrides and understand the role of hydrogen played on the metallicity. 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 role of hydrogen 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 2011, I have used all of the total allocated CPU time of 499,200 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 (Crystal structure AnaLYsis through Particle Swarm Optimization). 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. Result

We have explored the structures of calcium hydrides CaH_{2n} ($n = 2 - 6$). For each stoichiometry, calculations were performed at pressures 50-200 GPa with up to four formula units in the model. The enthalpies of candidate structures relative to the products of dissociation into $\text{CaH}_2 + \text{solid H}_2$ at the appropriate pressures are summarized in Fig. 1(a). The essential information can be summarized as follows: (i) except for CaH_{10} , stable structures began to emerge at pressures < 50 GPa; (ii) CaH_4 was the most stable phase at pressures between 50 and 150 GPa, while at 200 GPa CaH_6 had the lowest enthalpy of formation; (iii) the breakup of hydrogen molecules depended on the Ca/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. CaH_3 , CaH_5 , and CaH_7 , etc) were found to be energetically very unfavourable and were excluded in the discussions

The structures of the stable phases for each stoichiometry at 150 GPa are shown in Fig. 1(b)-(d). Three types of hydrogen species, “H4” units, monatomic H + H_2 , and molecular H_2 , were observed. CaH_4 had a tetragonal ($I4/mmm$, Pearson symbol $tI10$) structure and included a body-centred arrangement of Ca and two molecular and four monatomic hydrogen units ($\text{Ca}_2(\text{H}_2)_2(\text{H})_4$). The structure of CaH_6 adopted a remarkable cubic form ($Im\bar{3}m$, Pearson symbol $cI14$), with body-centred Ca atoms and, on each face, squared “H4” units tilted 45° with respect to the plane of the Ca atoms. These “H4” units were interlinked to form a sodalite framework with a Ca atom enclathrated at the centre of each cage. The next stable polymorph, CaH_{12} , had a rhombohedral ($R\bar{3}$, Pearson symbol

$hR13$) structure consisting entirely of molecular H_2 .

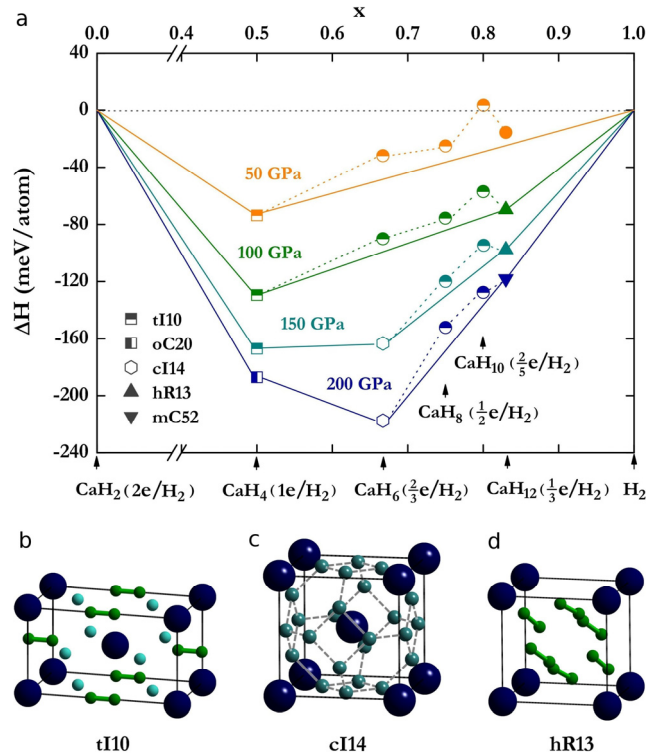


Figure 1 | Enthalpies of formation (ΔH , with respect to CaH_2 and H_2) of CaH_{2n} ($n=2-6$) and crystal structures. a. The abscissa x is the fraction of H_2 in the structures. The open, solid, and half-filled symbols indicate that the structures are composed of H_4 units, molecular H_2 , and the coexistence of H_2 and H, respectively. The metastable structures are

indicated by circles. The stable pressure ranges for CaH_4 , CaH_6 , and CaH_{12} are 50–200 GPa, 150–200 GPa, and 100–200 GPa, respectively. The EAE (per H_2) is shown in brackets. The estimated stability fields were determined according to the static enthalpies and may shift upon inclusion of dynamic effects (the zero-point motion of the nuclei). b. Structure of $tI10$ - CaH_4 . c. Structure of $cI14$ - CaH_6 . d. Structure of $hR13$ - CaH_{12} . Monatomic H, molecular H_2 , and Ca atoms are shown as cyan, green, and royal blue, respectively. The green cylinders and grey dashed lines are drawn to represent molecular H_2 and the sodalite cage, respectively.

The phonon dispersion curves, phonon linewidth $\gamma(\omega)$, EPC parameter λ , and Eliashberg spectral function $\alpha^2F(\omega)$ were calculated. A gap at 430 cm^{-1} (Fig. 2) separated the phonon spectrum into two regions: the lower frequency branches were associated with the motions of both Ca and H,

whereas the higher frequency branches were mainly associated with H atoms. The combined contribution (19% and 81%, respectively) gave an EPC parameter λ of 2.69. The calculated phonon linewidths (Fig. 2) showed that the EPC was derived primarily from the T_{2g} and E_g modes at the zone centre.

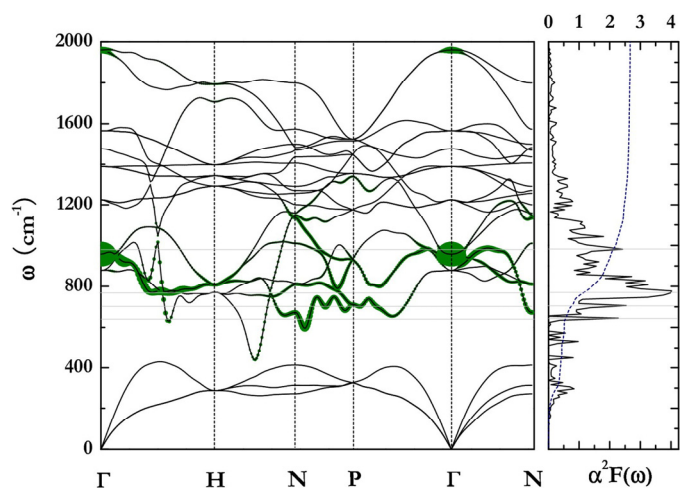


Figure 2 | Phonon band structure and Eliashberg spectral function. Phonon dispersion curves of cI14 at 150 GPa (left panel). Olive circles indicate the phonon linewidth with a radius proportional to the strength. Phonons with a larger linewidth at Γ belong to the t_{2g} and e_g modes, as indicated by the circles at 960 cm⁻¹ and 1960 cm⁻¹, respectively. Eliashberg electron-phonon coupling spectral function $\alpha^2F(\omega)$ at 150 GPa (right panel). Dashed line is the integration of the electron-phonon coupling strength as a function of phonon frequency. The horizon lines are drawn as a guide.

T_c was calculated based on the spectral function $\alpha^2F(\omega)$ by numerically solving the Eliashberg equations, which consist of coupled non-linear equations describing the frequency-dependent order parameter and renormalisation factor. The Coulomb repulsion is taken into account in terms of the Coulomb pseudopotential, μ^* , scaled to a cutoff frequency (typically six times the maximum phonon frequency). At 150 GPa, the predicted T_c values were 235 K and 220 K using typical values for μ^* of 0.1 and 0.13, respectively. EPC calculations were also

performed for 200 GPa and 250 GPa, in which the calculated T_c was found to decrease with pressure (201 K at 200 GPa and 187 K at 250 GPa for $\mu^*=0.13$), with a pressure coefficient (dT_c/dP) of -0.33 K/GPa. T_c of the order of 200 K is among the highest for all reported hydrides.

4. Conclusion

Through a systematic investigation of Ca hydrides with different hydrogen contents using particle-swarm optimization structural search, we show that in the stoichiometry CaH₆ a body-centred cubic structure with hydrogen that forms unusual “sodalite” cages containing enclathrated Ca stabilizes above pressure 150 GPa. The stability of this structure is derived from the acceptance by two H₂ of electrons donated by Ca forming a “H₄” unit as the building block in the construction of the 3-dimensional sodalite cage. This unique structure has a partial occupation of the degenerated orbitals at the zone centre. The resultant dynamic Jahn–Teller effect helps to enhance electron–phonon coupling and leads to superconductivity of CaH₆. A superconducting critical temperature (T_c) of 220–235 K at 150 GPa obtained from the solution of the Eliashberg equations is the highest among all hydrides studied thus far.

The formation of a hydrogen sodalite cage with enclathrated calcium in CaH₆, reported here for hydrogen-rich compounds, provides an unexpected example of a good superconductor created by the compression of a mixture of elemental calcium + hydrogen or CaH₂ + hydrogen. This novel superconductor can also be viewed as consisting of unique square “H₄” units and electron-donating calcium atoms subject to JT effects. Dense superconductive states, such as those reported here, may be favoured in other mixtures of elemental metals + hydrogen or any hydride + hydrogen upon compression. This work highlights the major role played by pressure in effectively overcoming the kinetic barrier to formation in the synthesis of novel hydrides.

RICC Usage Report for Fiscal Year 2011

5. If you wish to extend your account, provide usage situation (how far you have achieved, what calculation you have completed and what is yet to be done) and what you will do specifically in the next usage term.

I have been a RICC general user and wish to continue using the system. During the fiscal year 2011, I have performed systemically structure predictions, electronic band structures, phonons, electron-phonon calculations on CaHn (n= 4-8). Only part of the planed calculations on SrHn has been finished. For example, most of structural predictions on SrHn 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 2012, we plan to continue using RICC supercomputer to perform the rest of calculations on SrHn, then we will extend our research on the crystal structure prediction of MgHn and BaHn (n=1-8) through CALYPSO code, and build the zero pressure phase diagram. And eventually, to perform the electronic, phonons, and superconducting calculations for the thermodynamic stable structures of MgHn and BaHn (n=1-8). We expect high standard publications can be eventually achieved.

RICC Usage Report for Fiscal Year 2011

Fiscal Year 2011 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** (in press, 2012)

[Proceedings, etc.]

[Oral presentation at an international symposium]

[Others]