

Project Title:

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

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The significant advantage of the hydrogen rich materials in pursuing the high temperature superconductor is in its high Debye temperature due to the lightest atomic mass. Previously, the hydrogen rich materials of methane, silane, germane, and stannane have been suggested to be the possible high temperature superconductors under high pressure when they are metallic. Indeed, our theoretical calculations on silane and germane have revealed very high superconducting transition temperatures (T_c) of 55 K at 125 GPa and 64 K at 220 GPa, respectively. However, to further explore possible superconductivity in other hydrides, right crystal structures are considered as essential. Up to now, the crystal structures of methane and stannane under pressure are still open. We plan to systematically explore the crystal structures of these two hydrides based on the genetic algorithm in the crystal structure prediction and then to perform extensive electron-phonon coupling calculation using the predicted structures within the linear response theory in guiding the experimentally superconducting explorations.

Moreover, the alkaline earth metals, Ca, Sr, and Ba, (known as group IIA) possess a strong ability to donate electrons, but contain two electrons in the outermost energy level of their atoms. A larger electron transfer from alkaline earth metals to $H_2 \sigma_u^*$ than that of alkali metals can be expected, and this will directly increase the density of states near Fermi level (E_f). According to the McMillan formula, T_c is governed by three parameters: coupling-weighted phonon momentum (ω_{log}), electron-phonon coupling (λ), and conduction electrons near E_f . The

electron-phonon coupling will be large. Thus, the alkaline earth metals doped hydrogen may be new high-temperature superconductors at experimentally accessible pressures. Up to now, the thermodynamic properties of AH_n (A is alkaline earth metals) under pressure are still open. Therefore, it is interesting to study zero temperature phase diagram and the electron-phonon coupling of stable metallic phases for AH_n . Here, we have focused on our study on the hydrides of CaH_n, SrH_n, and BaH_n with n=4-8.

We run crystal structure predictions, structure optimization, and enthalpy calculations for SnH₄ and methane using USPEX, and for CaH_n using CALYPSO code and VASP code in RICC machine. After the enthalpy calculations for the selected structures, we then performed the phonon and electron-phonon coupling calculation using the PWSCF code for estimate of superconducting transition temperatures.

(1) **For stannane (SnH₄)**, we proposed the existence of two unique high-pressure metallic phases having space groups Ama2 and P63/mmc, which both contain hexagonal layers of Sn atoms and semimolecular (perhydride) H₂ units. In the Ama2 phase, Sn atoms form a simple hexagonal packing, where the trigonal prismatic holes are filled with semimolecular H₂ units (H-H distance 0.79 Å, which is longer than the 0.74 Å in the isolated H₂ molecule). The H₂ units are aligned either along the pseudo-hexagonal axis, or perpendicular to it, and these two orientations alternate (Fig. 1A). The P63/mmc phase here is based on the much denser hexagonal close packing of the Sn atoms (c/a 1.84 at

200 GPa, relatively close to the ideal value of 1.63). In this structure, the ordered H atoms are clearly split into two categories. One sort forms semimolecular H₂ units (the magenta atoms in Fig. 1B) occupying hexagonal channels of the hexagonal close packing structure, whereas the other sort of H atoms occupies positions just below and above Sn atoms, forming chains Sn-H...H-Sn-H...H-Sn-H running along the c axis (Fig. 1B). Enthalpy calculations (Fig. 2) reveal that the Ama2 and P6₃/mmc structures are stable at 96–180 GPa and above 180 GPa, respectively, while below 96 GPa SnH₄ is unstable with respect to elemental decomposition (Sn+H₂). The application of the Allen-Dynes modified McMillan equation reveals high superconducting temperatures of 15–22 K for the Ama2 phase at 120 GPa and 52–62 K for the P6₃/mmc phase at 200 GPa. The larger T_c in the P6₃/mmc structure is mainly attributed to the stronger λ of 0.87 and the larger ω_{log} of 1,135 K. The larger N(E_f) and higher intermediate frequencies in the phonon spectrum of the P6₃/mmc structure are probably responsible for the stronger λ. The current study will inevitably stimulate the future high-pressure experiments on the structural and conductivity measurements. These results have been published in *Proceedings of the National Academy of Sciences* **107**, 1317, (2010).

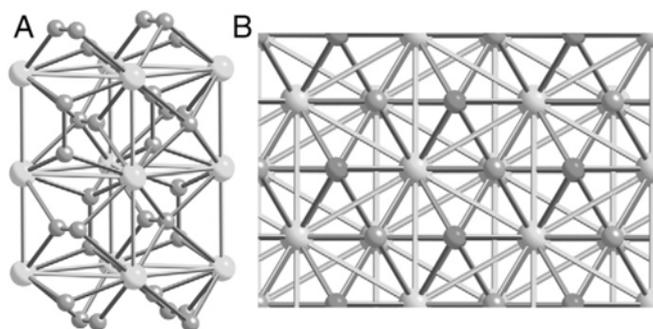


Figure 1. Ama2 (A) and P6₃/mmc (B) structures.

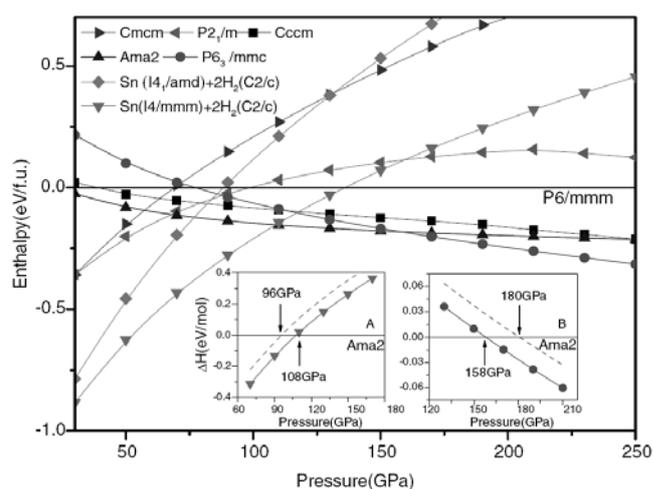


Fig.2 Enthalpy curves for the predicted structures. Ama2 and P6₃/mmc structures are stable at 96–180 GPa and above 180 GPa, respectively, while below 96 GPa SnH₄ is unstable with respect to elemental decomposition (Sn+H₂).

(2) **For methane (CH₄)**, its zero-temperature phase diagram under pressure has been systematically investigated, as shown in Fig. 4. At low pressure, methane keeps its molecular form and adopts P212121 symmetry below 78 GPa. In the range of 78-105 GPa, two novel structures with space groups Pnma and Cmcn are found to be the most promising candidates. Under higher pressure, methane becomes unstable and dissociates into the mixtures of C₂H₆, and C₄H₁₀ with hydrogen below 305 GPa, above which a mixture of diamond and hydrogen is stable. Our results also show that methane remains insulating up to very high pressures, which might be helpful to resolve the long-standing debate on the possibility of this compound as a superconductor within the reach of current high pressure techniques.

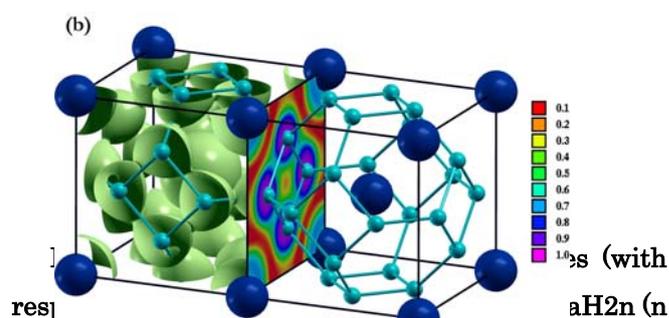
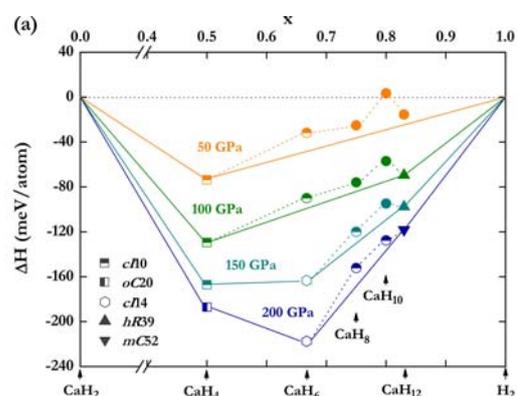
Since diamond, a decomposition product of methane, is denser than hydrogen and hydrocarbons, there should be gravitational precipitation of diamond inside giant planets Neptune and possibly Uranus. However, C₂H₆ and C₄H₁₀ do not precipitate. They may partly leak into the atmosphere. The complex transformation products, such as C₂H₆, C₄H₁₀, diamond and hydrogen, have to be

realistically taken into account in the models of internal evolution and energetic of these planets. These results have been published in [J. Chem. Phys. 113, 144508 \(2010\)](#).

(3) **For hydrogen-rich compound CaH_n**. Variable-cell simulations on crystal structure prediction through particle swarm optimization via our CALYPSO code with up to four formula units in the unit cell were performed for CaH_{2n} (n=1-6) at 50, 100, 150, and 200 GPa, respectively. Stable phases with all types of hydrogen configurations, pure H (*cI14*), H + H₂ (*tI10* and *oC20*) and H₂ unit (*hR39* and *mC52*), were predicted. The enthalpic trends and the general structural characteristics of the CaH_{2n} (n=2-6) phases are shown in Fig. 3a. The essential features of this diagram are the following: (i) stabilization begins to occur for all of the phases except CaH₁₀ at P < 50 GPa; (ii) CaH₄ is the most stable phase for P ≤ 150 GPa; at 200 GPa, CaH₆ is most stable; (iii) pressure to create H from H₂ increases obviously with the hydrogen composition; (iv) all H₂ units can be destructed by a pressure close to 150 GPa in CaH₆.

Although we have explored a variety of stoichiometries over several pressures, only one phase possessing pure H was found, CaH₆ (*cI14*, *Im-3m*), has a body-centered cubic (*bcc*) unit cell with H site at 12 *d* and Ca at 2 *a* position. A detailed DFT total energy calculation shown that *cI14* is the most stable phase of CaH_{2n} (n=1-6) at pressure above 155 GPa, and below which CaH₄ (*tI10*, *I4/mmm*) becomes most stable instead. The transition pressure further decreases to 148 GPa when the lattice zero-point energy is considered, and the details are reported here for 150 GPa. As shown in Fig. 1b, the H forms common 4- and 6-rings to give sodalite β-cages, while the Ca cations are located at the cage center. Each H is tetrahedrally coordinated by four nearest H. The H-H distance, *d*_{H-H}, is 1.238 Å at 150 GPa, far from the dimmer length (0.74 Å), but comparable to that (1.218 Å) of the second-nearest neighbors in

the hypothetical monatomic hydrogen (*tI4*, *I4₁/amd*) at 490 GPa, do suggest that *cI14* structure might display electronic similarities to that of monatomic hydrogen at approximately one third of the pressure to reach monatomic hydrogen itself. To the best of our knowledge, no such highly concentrated H configuration at pressure below, or close to, 150 GPa has been reported in any hydrides to date.



The abscissa *x* is the fraction of H₂ in the structures. A tie line may be used to connect two phases, and if the enthalpy of a third falls below it, the first two will react to give the third. Fig.3(b), The crystal structure of cI14 calculated at 150 GPa with ELF (Electron localization function) shown in the (100) plane, and the isosurface with ELF = 0.6.

(4) **For transition-metal diborides (TMB₂, TM = Sc, Ti, Y, and Zr)**. Besides the above materials, with the use of RICC machines, we also have obtained interesting scientific results on the high-pressure structures of transition metal diborides (TMB₂, TM = Sc, Ti, Y, Zr). We have extensively explored the high-pressure structures of transition-metal

diborides(TM=Sc,Ti,Y,andZr)

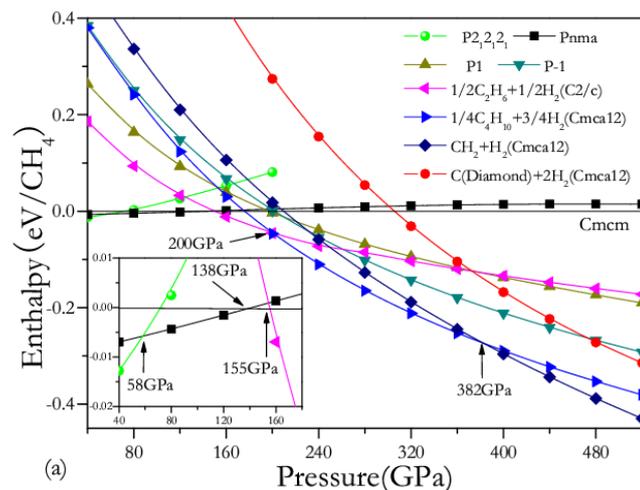


Fig. 4. Enthalpy curves (relative to our predicted *Cmc* phase) for CH_4 as a function of pressure

stabilized with the AlB_2 -type structure at ambient pressure by using first-principles structural prediction. We find two novel high-pressure structures: (i) a monoclinic structure ($\text{C}2/m$, $Z = 4$) for ScB_2 and YB_2 stable above 208 and 163 GPa, respectively; and (ii) a tetragonal R-ThSi_2 -type phase ($\text{I}41/\text{amd}$, $Z = 4$) for TiB_2 stable above 215 GPa. Our calculations show that the electron transfer from transition-metals TM to B under pressure might be the main cause for the structural phase transitions. Further phonon and hardness calculations suggest that R-ThSi_2 phase of TiB_2 is quenchable to ambient pressure and possesses excellent mechanical property with a Vickers hardness of 29.8 GPa. Interestingly, ZrB_2 is quite stable and persists on the ambient-pressure AlB_2 -type structure up to at least 300 GPa. We attribute the strong covalent hybridization between the transition-metal Zr and B to this ultrastability. Our research work has been published in [Inorg. Chem. 49,† 6859 \(2010\)](#).

In this year, I have encountered serious problems on the jobs running in RICC system. I am a Quick User and was allocated a total CPU hours of 804,000.00. However, due to the extreme low priority of Quick User in using RICC system, the major submitted jobs cannot get running. As a result, I only can use 182850.2 CPU hours, i.e., the only use of 22.7%

allocated CPU time. Therefore, to better use the RICC system, I plan to extend the use of RICC system as a General user for the calculation of hydrogen-rich compounds of CaH_n , SrH_n and BaH_n in next fiscal year.

Our planned schedule for further use of RICC system.

2011.04.01—2011.07.31: To finish the crystal structure prediction of CaH_n and SrH_n through CALYPSO code, and build the zero pressure phase diagram. During these three months, 210 evolutionary simulations (average 450 enthalpy calculations per simulation) will be performed, and it means that 94500 structures optimizations will be done.

2011.08.01—2011.10.31: To finish the electronic, phonons, and superconducting calculations for the thermodynamic stable structures of these hydrides. About 120 electron-phonon coupling calculations will be performed.

Fiscal Year 2010 List of Publications Resulting from the Use of RICC

[Publication]

[1] Guoying Gao, Artem R. Oganov, Peifang Li, Zhenwei Li, Hui Wang, Tian Cui, **Yanming Ma†**, Aitor Bergara, Andriy O. Lyakhov, **Toshiaki Iitaka**, and Guangtian Zou, “High-pressure crystal structures and superconductivity of Stannane (SnH₄)”, **Proc. Natl. Acad. Sci. USA** **107**, 1317 (2010).

[2] Guoying Gao, Artem Oganov, **Yanming Ma†**, Hui Wang, Peifang Li, Yinwei Li, **Toshiaki Iitaka**, and Guangtian Zou, “Dissociation of methane under high pressure”, **J. Chem. Phys.** **113**, 144508 (2010).

[3] Meiguang Zhang, Hui Wang, Hongbo Wang, Xinxin Zhang, **Toshiaki Iitaka**, **Yanming Ma†**, “First-Principles Prediction on the High-Pressure Structures of Transition Metal Diborides (TMB₂, TM = Sc, Ti, Y, Zr)”, **Inorg. Chem.** **49**,† 6859 (2010).

[Proceedings, etc.]

[Oral presentation at an international symposium]

[Others]