Project Title:

Prediction of Crystal Structure and Properties

Name: Yanming Ma, John Sak Tse, Zhi Li, Cheng Lu, ○Toshiaki Iitaka

Laboratory at RIKEN: Computational Astrophysics Laboratory

Recent research on the synthesis of hydrogen-rich binary metallic alloys at high pressure was stimulated by the proposal that these dense hydrogen alloys are potential superconductors with high critical temperatures, T_c. Indeed, very recently, a very high T_c of 190 K has been observed in hydrogen sulphide (H_2S) compressed to 200 GPa. During the fiscal year 2015, we have investigated several hydrogen-rich compounds by *ab initio* crystal structure predictions method and superconducting state have been found in a novel high-pressure polymorph of SiH_4.

We find that a three dimensional $P\bar{3}$ structure becomes the most stable phase above 241 GPa. A prominent structural feature, which separates the $P\bar{3}$ structure from previously observed/predicted SiH_4 structures, is that a fraction of hydrogen leaves the Si-H bonding environment and forms segregated H_2 units. The H_2 units are sparsely populated in the system and intercalated with a polymeric Si-H framework. Calculations of enthalpy of formation suggest that the $P\bar{3}$ structure is against the decomposition into Si-H binaries and/or the elemental crystals. Structural stability of the $P\bar{3}$ structure is attributed to the electron-deficient multicenter Si-H-Si interactions when neighboring silicon atoms are linked together through a common hydrogen atom. Within the multicenter bonds, electrons are delocalized and this leads to a metallic state, possibly also a superconducting state, for SiH_4. The estimated T_c turns out to be 32 K at 300 GPa. An interesting outcome of the present study is that the enthalpy sum of SiH_4 ($P\bar{3}$ structure) and Si (fcc structure) appears to be lower than the enthalpy of disilane (Si_2H_6) between 200 and 300 GPa (for all previously predicted crystalline forms of Si_2H_6), which calls for a revisit of the stability of Si_2H_6 under high pressure.

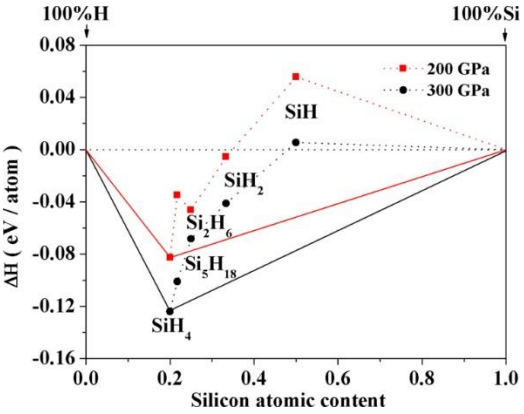

Fig.1. Enthalpy of formation ($\triangle H_f$, with respect to elemental crystals of H_2 and Si) for four Si-H stoichiometries calculated at 200 and300GPa.

Structural search was performed to investigate the phase stabilities and structures of SrH_{2n} (n = 1–5) in the pressure range 50–300 GPa. The high-pressure polymorphs reveal a variety of hydrogen structural units ranging from monatomic hydride to linear and bent H_3 and spiral polymer chains. A novel graphene like H-layer structure was found to exist in SrH_{10} at 300 GPa. The structural diversity in the predicted high pressure structures provides an opportunity for an in-depth analysis of the chemical bonding in the high pressure polyhydrides. It is shown from theoretical calculations that electronegativity of molecular hydrogen is similar to group 13 and 14 elements. This resulted in electrons being transferred from Sr to the hydrogen molecules. Thus, a consideration of the number of valence electrons available from Sr that can be shared among the H_2, serves as a useful guide to rationalize the structures of the H-moieties.

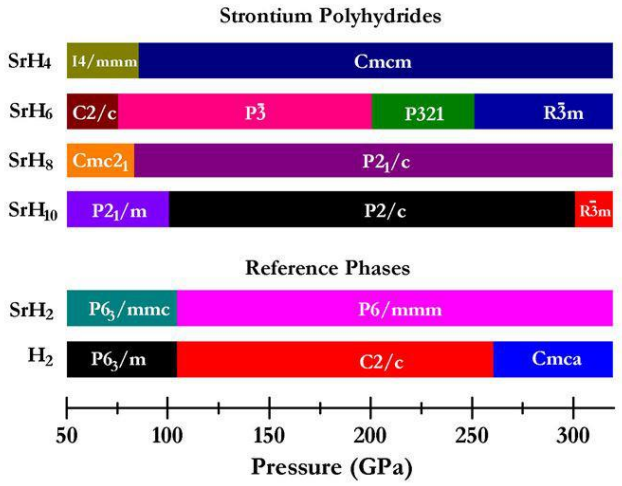

Fig.2. The phase transition sequences of strontium polyhydrides and the reference phases at pressures of 50 to 330 GPa.

Fiscal Year 2015 List of Publications Resulting from the Use of the supercomputer

[Publication]

Wenwen Cui, Jingming Shi, Hanyu Liu, Yansun Yao, Hui Wang, Toshiaki Iitaka and Yanming Ma, "Hydrogen segregation and its roles in structural stability and metallization: silane under pressure", Scientific Reports 5, 13039 (2015).
http://www.nature.com/articles/srep13039

Ziwei Wang, Hui Wang, John S Tse, Toshiaki Iitaka and Yanming Ma , "Stabilization of H3+ in the high pressure crystalline structure of HnCl (n = 2-7) ",Chem. Sci. 6, 522-526 (2015).
http://dx.doi.org/10.1039/C4SC02802C

Zhi Li, Jinwoong Kim, Nicholas Kioussis, Shu-Yu Ning, Haibin Su, Toshiaki Iitaka, Takami Tohyama, Xinyu Yang, Jiu-Xing Zhang, "GdN thin film: Chern insulating state on square lattice", Phys. Rev. B92, 201303 (2015).
http://dx.doi.org/10.1103/PhysRevB.92.201303

Jing-Jing Wang, Andreas Hermann, Xiao-Yu Kuang, Yuan-Yuan Jin, Cheng Lu, Chuan-Zhao Zhang, Meng Ju, Meng-Ting Si and Toshiaki Iitaka, "Exploration of stable stoichiometries, physical properties and hardness in the Rh-Si system: a first-principles study", RSC ADVANCES 5, 53497-53503 (2015).
http://dx.doi.org/10.1039/c5ra08476h