RICC Usage Report for Fiscal Year 2014

Project Title:

Prediction of Crystal Structure and Properties

Name: Yanming Ma,John Sak Tse,Zhi Li,○Toshiaki Iitaka
Laboratory at RIKEN: Computational Astrophysics Lab

---

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

The recent discovery of the phase IV of hydrogen—a mixed structure composed of layers of molecular units as well as weakly bonded graphene-like sheets—has generated much excitement. However, solid hydrogen remains insulating at pressure up to at least 320 GPa, and thus its potential superconductivity is still beyond realization. As an alternative, hydrogen-rich group IV hydrides (i.e., CH_4 , SiH_4 , GeH_4 , and SnH_4) are extensively explored since their metallization can happen at much lower pressures accessible to current experiments.

Recent experiments have demonstrated that these hydrogen-rich full-shell group IV hydrides (CH_4 and SiH_4) can adsorb additional H_2 molecules at high pressures forming a series of new H_2-containing compounds, e.g., $CH_4(H_2)_2$, $(CH_4)_2H_2$, $CH_4(H_2)_4$, CH_4H_2, and $SiH_4(H_2)_2$. In a further survey of literatures, H_2 was even found to interact with H_2O, NH_3BH_3, Ar, and Xe at readily accessible pressures stabilizing at stoichiometric compounds. The exploration of high-pressure metallization of these compounds is greatly desirable in search of high-temperature superconductors since here the demanding H_2 units automatically apply. We explored the high-pressure structures of $SiH_4(H_2)_2$ in the pressure range 50–300 GPa. An intriguing layered metallic structure was revealed to be energetically stable above 248 GPa with the inclusion of zero-point energy. Application of the Allen-Dynes modified McMillan equation yields remarkably high superconducting temperatures of 98–107 K at 250 GPa, among the highest values reported so far for phonon- mediated superconductors.

The simple molecular solids formed by diatomic molecules, hydrogen halides H_nM, (M=Cl, Br and I, n=1) possess strong to modest hydrogen bonds and have attracted much attention for decades. It is well accepted that pressure can efficiently revise the bonding properties of materials, including hydrogen bonds containing systems. It is thus expected that upon compression the abundant bonding changes in hydrogen halides could occur and may open the opportunity to adsorb additional H_2 molecules at high pressures forming a series of new H_2-containing compounds. Computational studies of the structural, electronic and superconductive properties of polyhydrides of them are thus of great interests.

It is found that HCl and HBr become metallic at 130 GPa and 80 GPa, respectively. However, superconductivity has not yet been found in those materials. As has been shown in ployhydrides $SiH_4(H_2)_2$ by previous investigations, a large amount of additional hydrogen atoms is very likely to 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 ployhydrides with only a little bit of halogens may be new high-temperature superconductors at experimentally accessible pressures. Up to now, the thermodynamic and superconductive properties of H_nM (M are halogens) 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 H_nM. Here, we will focus our study on the hydrides of HnCl, H_nBr and H_nI with $n \geq 2$.

2. Specific usage status of the system and calculation method

During the fiscal year 2014, We have used more than 98% 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. Result

The relative energetics of the H-Cl system with H-rich stoichiometry from 100 to 300 GPa are summarized in the convex hull plot shown in Fig. 1. The enthalpies of formation were evaluated as the difference in the enthalpy of predicted H_nCl structure with solid HCl and H_2 at the selected pressures. Since hydrogen has a small atomic mass, zero point energy (ZPE) may be important. To investigate the vibrational effects on the phase stability, ZPEs for H_2Cl and H_5Cl were estimated at 100–300 GPa from the corresponding phonon spectra using the quasi-harmonic approximation.[29] It is found that the ZPEs are quite small and the inclusion of ZPEs in the phase diagram only resulted in a slight shift in the formation pressures but the stability of both phases remains unaltered. Structures lying on the convex hull are thermodynamically stable or metastable and, in principle, can be synthesized. Fig.1 reveals that only two HCl-H_2 complexes, H_2Cl and H_5Cl are stable at 100GPa. At this pressure H_2Cl has the most negative enthalpy of formation. With increasing pressure, the stability of H_5Cl relative to H_2Cl increases and becomes the most stable phase at 300 GPa.

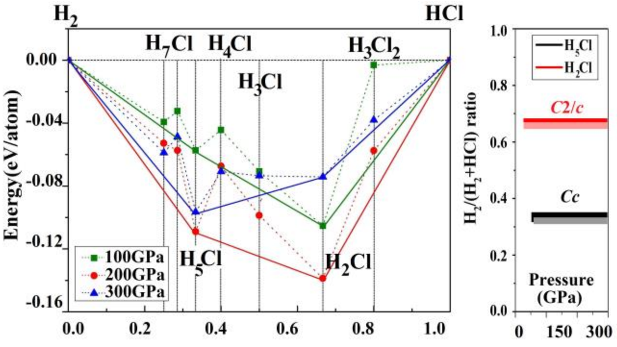

Figure 1. **Stability of new hydrogen chlorides.** (*A*) Enthalpies of formation (ΔH, with respect to HCl and H_2 of their most stable phases at selected pressures) of H_nCl (n = 1–7). The abscissa x is the fraction of H_2 in the structures. Circles lie on the solid lines represent stable ground-state compounds under corresponding pressure. (B) Pressure-composition phase diagram of the H-Cl system. Light colored lines represent the vdW corrections to corresponding structures.

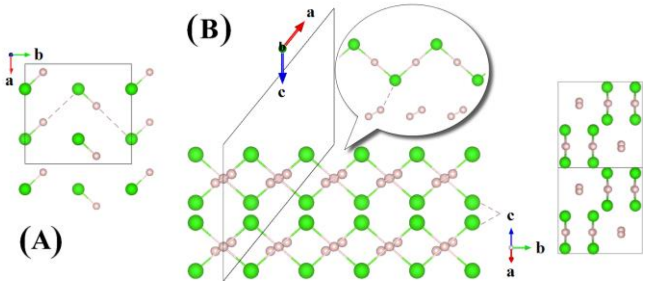

Figure 2 **Crystal structures of hydrogen chlorides.** (A) Experimental structure of HCl at ambient pressure low temperature, (B) *C*2/*c*-H_2Cl recovered at 100 GPa along different angle

vdW effects may play an important role in stabilization of a molecular solid. We have thus performed additional calculations on the H-Cl system with the vdW-DF2 method[26]. The results show the differences between calculations with and without vdW corrections on the formation enthalpies of the structures considered in Fig. 1 are small. The formation pressures were found to change slightly. For example, the stabilized pressure of H_2Cl was increased from 21.2 to 21.3 GPa, while for H_5Cl it increased from 50 to 60 GPa. Otherwise, the energetic order remains the same.

Now we examine the development of the high pressure crystal structures in H_nCl (n =2-7). The starting point is the crystal structure of HCl under ambient pressure. At low temperature, x-ray and neutron diffraction show HCl crystallized in an orthorhombic structure ($Bb2_1m$).[30] In the crystal, HCl molecules are linked via the H atoms forming zigzag chains running parallel to the crystallographic ***b*** axis. The nearest neighbour Cl-H and second nearest neighbour Cl…H distances are 1.25 Å and 2.44 Å, respectively. The Cl…Cl separation is 3.88 Å. And the H-Cl…H valence angle is 93.6°. The predicted crystalline phase of H_2Cl at 100 GPa has a $C2/c$ space group and the structure is shown in Fig. 2. The crystal is formed from HCl chains interposed with H_2 molecules. In this case, the H in the HCl chain is midway between the two Cl atoms with an H-Cl distance of 1.45 Å. The H-Cl-H angle has opened to 97.9° and the Cl…Cl separation is shortened to 2.90 Å. The H_2 units in the structure all have a H-H distance of 0.74 Å, which almost identical to that of the isolated molecule. The Bader charges for the H in the chain and Cl atoms are +0.44 and -0.35, respectively and 0.0 for the H atoms in the H_2 units. The closest contact between a Cl atom and the H_2 molecule is 1.98 Å. The crystal structure of H_2Cl at 300 GPa differs little from that at 100 GPa. The H atoms in the H-Cl chains still situated at the middle of two neighbouring Cl atoms with a H-Cl distance of 1.35 Å. The H-Cl-H angle is 95.5° and the shortest separation between two Cl atoms has reduced further to 2.69 Å. The H-H bond length in the H_2 unit is 0.73 Å. The closest H_2…Cl distance is. 1.70 Å. Compression has a significant effect on the interatomic distances of the H-Cl chains but does not alter fundamentally the underlying bonding pattern. A longer H-Cl distance in the chain suggests increased ionicity of the Cl-H bonds.

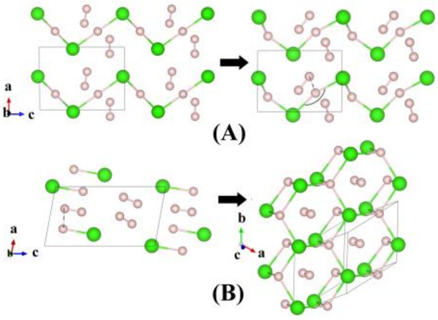

Figure 3 **Crystal structures of hydrogen chlorides.** Predicted metastable pase H_3Cl (A) and H_4Cl (B) from pressure 100 to 300 GPa.

Although H_3Cl and H_4Cl are only metastable, it is instructive to examine the evolution of the crystal structure with increase H_2 concentration. The structures of H_3Cl at 100 and 300 GPa are shown in Fig. 3. Both are composed of zigzag H-Cl chains. Like H_2Cl, the H atom is equidistant from the two nearest Cl atom with H-Cl bond distance of 1.44 Å at 100 GPa and 1.43Å at 300 GPa. The most significant difference between the low and high pressure structures is that the Cl-H-Cl angle is almost linear at 100 GPa but bend to 135° at 300 GPa. At 300 GPa, the closest contact between the H_2 and the H in the chain is 1.27 Å. However, in both cases, the H-H distance of the H_2 molecule remains to be 0.73 Å. The structure of H_4Cl at 100 GPa differ dramatically from all the structures within this series of compounds. Instead of H-Cl chains, the structure is composed of isolated HCl and H_2 molecules. The

H-Cl distance is 1.38 Å and the H-H bond length is 0.74 Å. For comparison, the H-Cl bond of a free molecule is 1.276 Å. Therefore, the distance in the solid at 100 GPa is slightly longer. The structure of H_4Cl at 300 GPa again is different from that at 100 GPa. The basic building units are isolated Cl atoms, H_2 molecules with H-H distance of 0.74 Å and a novel 2-D layer of slightly puckered fused hexagonal rings formed from 3 HCl units with additional H atoms attached to the Cl atoms. Each H atom in the ring is bonded to three Cl atoms. In addition, each Cl is bonded to an extra H atom which is not coordinate to other species in the crystal. The H-Cl distances in the fused ring are 1.59 Å and the terminal H-Cl is substantially short at 1.49 Å. Interestingly, the terminal H-Cl-H (ring) angles are 77° and the in-plane H-Cl-H and Cl-H-Cl angles are between 114-115°.

An interesting structure was observed in H_5Cl at 100 GPa. Although chains formed from Cl and H atoms are still clearly visible, the detail construction of the chain is very different. In H_5Cl, instead of placing one H atom midway between two nearest neighbour Cl atoms, it is replaced by an H_3 unit. The H_3 is a distorted isosceles triangle and can be described as a loosely bound unit of an H atom and an elongated H_2 with an apical angle of 63.8°. The apical H atom is linked to two nearest Cl atoms in the chain with H-Cl distance of 1.47 Å. The distances from the apical H atom to the two H forming the H_2 are 1.01 Å and 0.97 Å, respectively and the intermolecular H-H distance is 0.81 Å. The remaining H_2 units in the structure have H-H distances of 0.74 Å. Moreover, the shortest distance from these H_2 to the H_3 is 1.36 Å and, therefore, may be considered as non-interacting molecules.

Compression of H_5Cl to 300 GPa does not change the space group symmetry. The chain pattern with interpose H_3 units is still maintained, but the local H…H interactions have changed dramatically. The H_3 unit now approaches an equilateral triangle. The H-H lengths are 0.87, 0.87 and 0.88 Å with bond angles 59.7, 59.7 and 60.5°. The Cl-H distance has elongated from 1.47 Å at 100 GPa to 1.60 Å! The large lengthening of the Cl-H clearly suggests a substantial change in the Cl-H bonds. More significantly, the isolate H_2 molecules are now pushed towards the H_3 units and interact with one of the H atoms forming two almost H…H bonds at 1.15 Å. Concomitantly, the distance in H_2 is lengthened to 0.76 Å. The Bader charges for the H atom in the H_3 and H_2 units and for the Cl atom are +0.16 and +0.014 and -0.48 respectively. In comparison to H_2Cl the ionicity on both the H and Cl atoms have increased substantially. A plot of the electron localization function (ELF) shown in Fig. 4 shows localized spin paired electron density within the H_3 ring and in the H_2 molecule (ELF over 0.8). Weak pairing also observed between one of the H in the H_3 ring with the two H atoms of H_2.

It is tempting to relate the positively charged H_3 unit to an isolated trihydrogen cation H_3^+. H_3^+ has a perfect triangular structure with H-H bond distance of 0.90 Å. For comparison, at 300 GPa the average intramolecular H-H distance in the H_3 unit in H_5Cl is 0.87 Å and a total charge of +0.48 (3×0.16). In addition, the H-H distance of 0.76 Å in the H_2 unit is only slightly perturbed from the isolated molecule. Therefore, it is not unreasonable to suggest that high pressure H_5Cl structure is composed of H_3^+ stabilized in the solid states through primarily ionic interaction with the Cl atoms and secondary weak interaction with a pair of H_2 molecule. To investigate further properties of the H_3^+ unit in H_5Cl, the phonon densities of states calculated at 300 GPa is shown in Figure 5. The low-energy vibrations from 100–500 cm^{-1} are dominated by the Cl atomic motions. The phonon modes in the region from 1800 to 3400 cm^{-1} can be assigned to H_3^+ molecular vibrations and then near 4000 cm^{-1} to the H_2 molecule. The H_3^+ bend vibrations are split into two bands centered at 1800 cm^{-1} and 2000 cm^{-1}. The peak at 3350 cm^{-1} is attributed to the stretching vibration. In comparison, the fundamental frequencies for isolated H_3^+ are v (stretch) = 3220·48 cm^{-1} and v (bend) = 2545·99 cm^{-1}, the latter is a degenerated mode[31]. The vibration frequency is 4350 cm^{-1} for a free H_2 molecule. The main mechanism for the synthesis of H_3^+ by experiment is via the chemical reaction[32]: $H^+ + H_2 \rightarrow H_3^+$. The concentration of H_2^+ is the limiting factor on the rate of this reaction. H_2^+ can only be produced in interstellar space by the ionization of H_2 by a cosmic ray. In H_5Cl, the electronegative chlorine atoms acquire electrons from the hydrogen. From previous studies, it is known that high pressure facilitates the transfer of electrons from the more electropositive element into the interstitials of a crystal forming electrides. In this case, these electrons, being transfer to the chlorine, are originated from the hydrogen. The formation of multicenter $H_3...H_2$ clusters helps to delocalize the positive charge and stabilizes the system. This explains the unexpected formation of H_3^+-like units in the crystal structure.

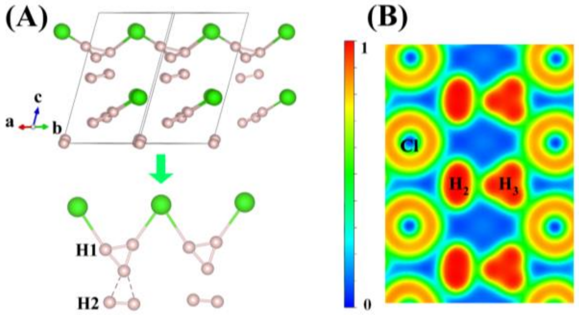

Figure 4 (A) **crystal structure** of *Cc*-H_5Cl recovered at 100 GPa and its chain style when compressed to 300 GPa. (B) **Electron localization function (ELF) maps** of the planes where the hydrogen and chloride atoms lie for the *Cc* structure at 300 GPa.

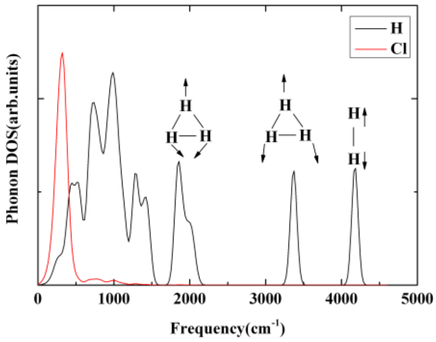

Figure 5 **The phonon densities of states** for *Cc*-H_5Cl at 300 GPa is shown. The modes corresponding to the triatomic H_3^+ stretch, as well as the H_2 vibron are denoted.

The nature of bonding in the group 17 hydrides at high pressure is different from group 1 and 2 and group 14 hydrides. One observed a gradual shift in the chemical interaction from electron transfer in electropositive group 1 and 3 compounds to covalent bonding group 14 and finally the ionic bonding in group 17 elements. Although this study was focused on Cl, we anticipate a similar bonding mechanism is applicable to other halogen hydrides.

4. Conclusion

We have investigated the phase stability of the HCl-H_2 system at high pressure using the PSO algorithm in combination with *ab initio* density functional based electronic calculations. Between 100 – 300 GPa, two stable phases with the H_5Cl and H_2Cl stoichiometries were found. The basic structure of the high pressure phases is similar to the low temperature ambient pressure structure of HCl. H_2Cl is consisted of zigzag H-Cl chains and non-interacting H_2 molecules. The most usual and informative finding is that while the chain like structure is preserved in H_5Cl, the H atoms connecting the Cl in the chains are replaced by units consist of weakly interacting $H_2...H_3$. The H_3^+ is positively charged and stabilized from the formation of multicenter bonds. The similarity in the local structure, vibrational frequencies and electronic charge compel us to relate the unit to the isolated H_3^+ molecule. It is also found that the effect of pressure on the electronic structure of group 17 hydrides is very different from the more electropositive group 1 and 2 elements: the electron-rich Cl atom and anion do not transfer their electrons into interstitial space of the crystal under very high compression. In fact electrons are removed from the H atoms leading to the formation of cationic clusters that benefit from multicenter bonding.

５. Schedule and prospect for the future

We have been a RICC general user and wish to continue using the system. During the last fiscal year 2014, We have finished the studies of H_nCl, $n \geqslant 2$, and got 2 papers published on Chem. Sci. and J. Chem. Phys., respectively. However, only part of the planed calculations on H_nI and H_nBr ($n \geqslant 2$) have been finished. For example, most of structural predictions on H_nI (n=1-6) were done. But the calculations on H_nBr and the electronic structures of H_nI have not been completely finished yet. For the next fiscal year 2015, we plan to continue using RICC supercomputer to perform the rest of calculations on H_nI and H_nBr, then we will extend our research to the crystal structure predictions of other systems, e.g. MoH_n ($n \geqslant 2$) and SiH_4, through CALYPSO code, and build the high pressure phase diagram. We expect high standard publications can be eventually achieved.

RICC Usage Report for Fiscal Year 2014

Fiscal Year 2014 List of Publications Resulting from the Use of RICC

[Publication]

1. Ziwei Wang, Hui Wang†, John S. Tse†, Toshiaki Iitakad and Yanming Ma,"Stabilization of H_3^+ in the high pressure crystalline structure of H_nCl (n = 2–7) "**Chem. Sci. 6** , 522 (2015)
2. Ziwei Wang, Yansun Yao, Li Zhu, Hanyu Liu, Toshiaki Iitaka, Hui Wang and Yanming Ma†, "Metallization and superconductivity of BeH_2 under high pressure", **J. Chem. Phys. 140**, 124707 (2014).