Project Title:

First priniciple calculations of the "Missing Xenon Problem"

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

The reactivity of noble gas elements is important for both fundamental chemistry and geological science. The discovery of the oxidation of Xe extended the doctrinal boundary of chemistry that a complete shell is inert to reaction. The oxidations of Xe by various geological substances have been researched in order to explain the missing Xe in earth atmosphere. Among many proposals, the chemistry mechanisms are straightforward as they identify chemical processes that can capture Xe in earth interior. However, all the mechanisms based on current noble gas chemistry face the same difficulty: the earth lower mantle and core are rich in metals and therefore their chemical environment is reductive. On the other hand, up till now, the opposite chemical inclination-the reductive propensity, i.e. gaining electrons and forming anions, has not been proposed and examined for noble gas elements. In this work, we will demonstrate, using first principles calculations and an efficient structure prediction method, that Xe can form stable Si-Xe or Al-Xe compounds under high pressure. We also find that elevated temperature has large effect in stabilizing Al-Xe compounds. Our results show that the earth has the capability of capturing Xe, which is consistent to the depletion of Xe in earth atmosphere.

2. Specific usage status of the system and calculation method

Our structure prediction is based on a global minimum search of the free energy surfaces obtained by ab initio total-energy calculations, through CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology. The significant feature of this methodology is the capability of predicting the stable structure with only the knowledge of the chemical composition at given external condition (for example, pressure). It has been successful in correctly predicting structures for various systems including elements, binary and ternary compounds. The evolutionary variable-cell structure predictions are performed at 0, 50, 100 , 150 and 250 GPa with one to six Si_xXe_y (Al_xXe_y) formula units (f.u.) per cell. Each generation contain 30 structures, 60% of which are generated by particle swarm optimization. The others are new and will be generated randomly. We followed 50 generations to achieve the converged structure.

The underlying ab initio structural relaxations and electronic calculations are carried out using density functional theory within the Perdew-Burke-Ernzerhof (PBE) exchange-correlation as implemented in the VASP (Vienna Ab Initio Simulation Package) code. The frozen-core all-electron projector-augmented wave method have been adopted. The cutoff energy of 1000 eV for the expansion of the wave function into plane waves and fine Monkhorst-Pack k meshes are chosen to ensure that all the enthalpy calculations are well converged to better than 1 meV/atom. The phonon calculations are carried out by using a supercell approach as implemented in the PHONOPY code. Raman and IR spectrum calculations have been carried out using a plane-wave pseudopotential scheme within linear response density-functional theory as implemented in the Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and Optimization) package. Forces and stresses for the converged structures are optimized and checked to be within the error between the VASP and Quantum-ESPRESSO code. The generalized gradient approximation of the

exchange-correlation function is employed. The electronic wave functions and the electron density are expanded by the plane-wave basis sets with a cutoff energy of 120 Ry. The Raman intensities were computed from the second-order derivative of the electronic density matrix with respect to a uniform electric field.

3. Result

Because the Earth's inner core is rich in both Si and Al, we mainly focused on the exploration of Xe–Si/Al compounds in the Si/Al rich regime. We therefore investigated the chemical stabilities of various Si_xXe_y and Al_xXe_y (x:y=1:6 to 6 : 1) compounds by calculating their formation enthalpies at 0 K and at pressures of 0, 20, 100, 200, 300 and 400 GPa, relative to the products of their dissociation into constituent elements, as summarized in Fig. 1. Other stoichiometries of Si_xXe_y with the half integer values of 1.5, 2.5, 3.5, 4.5 and 5.5 were also considered, but no new stable structures were found.

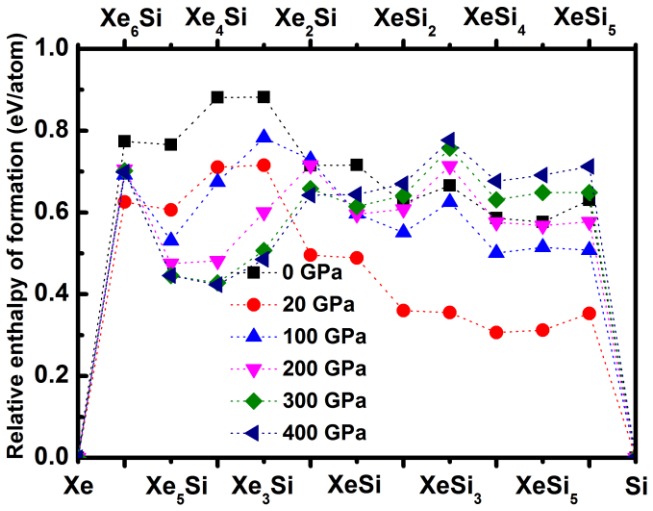

Fig. 1. Stability of Si_xXe_y compounds under pressure.

4. Conclusion

The Si_xXe_y compounds under pressure are not stable.

5. Schedule and prospect for the future

1. In the next year, we will demonstrate, using first principles calculations and an efficient structure prediction method, that Xe can form stable Al-Xe compounds under high pressure.

2. Methane hydrate is a possible substantial future energy resource. Despite the industrial implications and worldwide abundance of methane hydrates, the high pressure behaviors of these compounds remains poorly understood. In the next year, using an unbiased structure search method based on particle swarm optimization algorithm in conjunction with first-principles calculations, we systematically study the structural evolution of CH4(H2O)2 gas hydrates under high pressure up to 100 GPa.