Building a Chemical Intuition Under Pressure: Predictions of Novel Hydrides

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Abstract

Stabilization of phases with unusual combinations or stoichiometries, and unexpected electronic structures may be achieved by applying external pressure. The prediction of these structures using our chemical intuition (developed at 1 atmosphere) would be exceedingly difficult, making automated structure search techniques prudent. For this reason, we have written XTALOPT, an open-source evolutionary algorithm for crystal structure prediction.

Whereas at 1 atmosphere the classic alkali hydrides combine in a one-to-one ratio, M^+H^-, under pressure non-classic stoichiometries $MH_n (n > 1)$ and M_mH $(m > 1)$ are preferred. For example, theoretical work has predicted that LiH_6 and NaH_9 become particularly stable phases at about 100 and 25 GPa, respectively. And the potassium, rubidium and cesium polyhydrides all contain the H_3^- anion, the simplest exaple of a three centered four electron bond. The alkaline-earth polyhydrides are considered as well.

Chemical trends relating the stabilization pressure to the ionization potential, and the nature of the hydrogenic sublattice to the strength of the metal-hydride interaction can be made. These hydrogen-rich materials with nontraditional stoichiometries are computed to undergo an insulator to metal transition at pressures attainable in diamond anvil cells. It may be that these systems are superconductors at experimentally achievable pressures. The metal-rich region of the alkali/hydrogen phase diagram under pressure shows that alkali-metal subhydrides may also be stabilized under pressure.