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Pressure–Stabilized Sodium Polyhydrides, NaH_n ($n > 1$)

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Computations on NaH_n , $n = 6 - 12$, show that NaH_9 is stable by $P = 25$ GPa. $Cmc2_1$ - NaH_9 containing both H_2 and H^- units is metallic at $P > 250$ GPa. Other phases with only H_2 units metallize at lower pressures as a result of the partial filling of the H_2 σ_u^* bands by the Na $3s$ electrons. Pressure induced overlap of the Na $2p$ cores forestalls closure of the band gap in the odd–phases with H^- atoms, but the even–phases remain good metals up to 300 GPa. The lower the IP of the metal, the lower the pressure at which MH_n with $n > 1$ become stable. The larger the radius of M, the greater the optimal value of n .

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Perhaps the most compelling reason for an extended system to contain a large fraction of the first element is the prediction that metallized hydrogen [1] and hydrogen–rich compounds [2] may be high–temperature superconductors. Pressure can be employed to induce compound formation, and recent experiments have shown that at a number of H_2 containing van der Waals compounds such as $\text{Si}_4\text{-H}_2$ [3, 4], and Xe-H_2 [5] are formed. Theoretical work has focussed primarily on $\text{SiH}_4(\text{H}_2)_2$ which was predicted to metallize at pressures somewhat lower than that of pure H_2 , between 200–250 GPa [6].

Computations have illustrated that another class of hydrogen rich compounds — the alkali polyhydrides — may be stable as well [7]. At normal pressures, all of the alkali metals combine in a one–to–one ratio with hydrogen. Because of their low ionization potentials (IP), the alkali metals donate their valence s electrons to hydrogen yielding an ionic solid: M^+H^- . However when squeezed, LiH_n alloys with $n > 1$ are found to be stable [7]. The pressure necessary to form these phases was computed to be higher than that for the aforementioned van der Waals compounds, at least 100 GPa, but the stable systems were metals or semimetals. Metallization was found to occur via one of two mechanisms: (i) the formation of an H^- impurity band between the H_2 σ_g and σ_u^* bands (as in LiH_2), or (ii) partial filling of the H_2 σ_u^* bands by the Li $2s$ electrons (as in LiH_6).

The prediction of new materials using global search techniques such as evolutionary algorithms (EAs) as implemented in e.g. USPEX, and random structure searching e.g. AIRSS, have shown that computational structure prediction is a valuable tool especially for H–rich solids [7, 8]. In order to determine if the heavier alkali polyhydrides, NaH_n with $n > 1$, may also be stabilized under pressure, we have employed an open–source EA, XtalOpt [9], to predict the most stable structures up to pressures of 300 GPa [10]. The results of our calculations shed light on the effect of the lower IP (5.1 vs 5.4 eV) and larger ionic radius of sodium versus lithium on the geometries and electronic structures of the stable phases.

In elemental solids the heavier members of a group often follow the same structural changes as the lighter ones

but at reduced pressures [11]. For example, consider the classic alkali hydrides crystallize in the rocksalt structure at ambient pressures. NaH transforms to the CsCl structure at 29.3 GPa [12] (we calculate the transition to occur at ~ 37 GPa, see the Supplementary Information, SI [13]) whereas for LiH the transition is predicted to occur at 329 GPa [14]. As a first order prediction it may be reasonable to guess that for a given n the preferred NaH_n compounds will have the same structures as LiH_n , but they will be stabilized at lower pressures. As illustrated below, for the hydrides with non–traditional stoichiometries, the IP and the core size have a much more profound effect than expected.

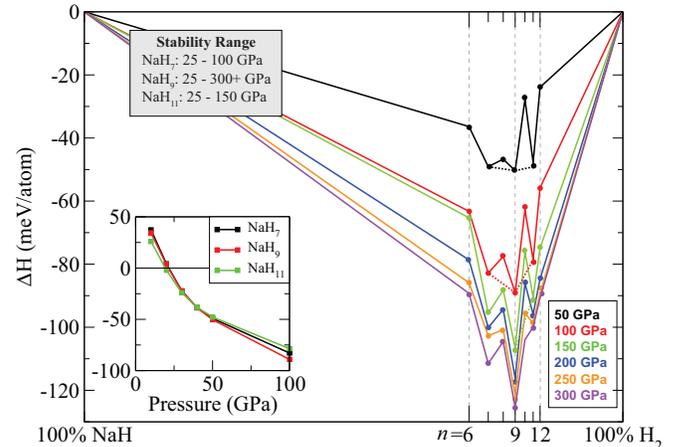


FIG. 1: (color online) Enthalpies of formation (ΔH_F , with respect to NaH and H_2) of the most stable NaH_n ($n = 6 - 12$). The grey inset shows the range of the thermodynamically stable phases, NaH_7 , NaH_9 and NaH_{11} , which become viable at ~ 25 GPa (white inset). The estimated stability fields were determined with static enthalpies and may shift upon inclusion of dynamical effects (the zero–point motion of the nuclei).

The enthalpic trends of the NaH_n ($n = 6 - 12$) phases studied are shown in Fig. 1, a tie–line representation. At all of the pressures considered, NaH_9 was computed as having the most negative ΔH_F . This stoichiometry is predicted to become stable at ~ 25 GPa (see the inset),

and remains thermodynamically preferred up to at least 300 GPa. NaH_7 and NaH_{11} , were found to be thermodynamically stable as well, but in a smaller pressure range of about 25-100 GPa and 25-150 GPa, respectively.

Our computations predict that NaH_n ($n > 1$) become stable at about $1/4^{\text{th}}$ of the pressure necessary to form LiH_n . This is likely due to the lower IP, and therefore enhanced reactivity of Na. Whereas LiH_6 was found to have the most negative ΔH_F of all of the LiH_n structures studied, the most stable sodium polyhydride is NaH_9 . We attribute this behavior to the larger radius of Na^+ as compared to Li^+ (0.99 vs. 0.59 Å for four-coordinate, 1.02 vs. 0.74 Å for six-coordinate [15]). Interestingly, the ratio of the number of H atoms in the most stable alkali polyhydride correlates well with the average ratio of the ionic-radii of the two alkali metals. This line of reasoning leads to the prediction that under pressure KH_x , RbH_y , and CsH_z with $x = 11 - 12$, $y = 12 - 13$ and $z = 14 - 15$ may be the most stable (see the SI). Other factors such as the low lying d -bands may also play an important role in determining the peculiarities of the heavier MH_n .

Supercells of the thermodynamically stable NaH_n phases are illustrated in Fig. 2. All of these consisted of an Na^+/H^- lattice (one hydridic hydrogen per Na) within a sea of H_2 molecules. As shown in the SI, the zero-point energy of the two distinct NaH_9 structures is comparable to the difference between their enthalpies, suggesting the possibility of liquid-like behavior of the hydrogen sublattice [16]. In fact, our computations indicate that this may also be the case for the hydrogen-rich NaH_8 and NaH_{10} phases discussed below.

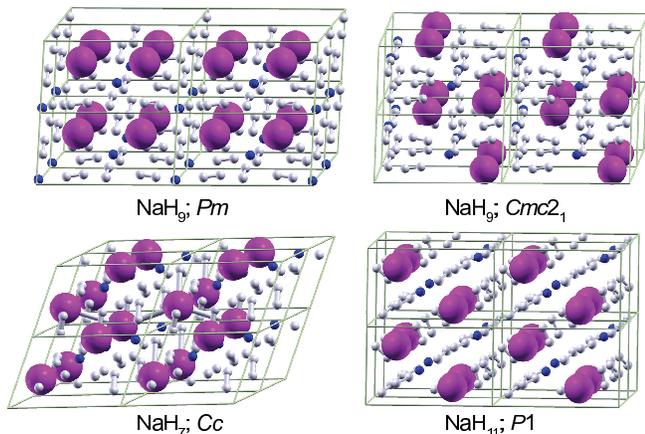


FIG. 2: (color online) $2 \times 2 \times 2$ supercells of the Cc - NaH_7 , Pm - NaH_9 and $P1$ - NaH_{11} systems stable at 100 GPa, as well as the $Cmc2_1$ - NaH_9 phase stable at 300 GPa. Na atoms are shown as purple, H atoms comprising H_2 units are white, and hydridic (H^-) hydrogens are blue. Phonon calculations carried out using VASP on supercells of 128 (NaH), 189 (NaH_6), 128 (NaH_7), 144 (NaH_8), 160 (NaH_9), and 88 (NaH_{10}) atoms indicated that these are local minima (see the SI). Phonon calculations on $P1$ - NaH_{11} were prohibitively expensive.

For $P < 25$ GPa, ionic attraction between Na^+ and the negatively charged atoms in the hydrogen sublattice give rise to Madelung precompression. However, because of the large Na^+ core, by 50 GPa the volume (per H atom) of the NaH_9 unit cell is already greater than that of an H_2 lattice. This is in complete analogy to previous results for LiH_n , where Madelung precompression was found to be effective only in the low-pressure regime.

The presence of H^- (blue in Fig. 2) suggests that the electronic structure of the sodium polyhydrides with odd stoichiometries will be similar to LiH_2 . Indeed, at 1 atm the densities of states of NaH_7 (Cc), NaH_9 (Pm , $Cmc2_1$) and NaH_{11} ($P1$) reveal an H^- impurity donor band falling between the H_2 σ_g and σ_u^* bands. At normal pressures, these phases are all insulating.

Despite the fact that at 1 atm the presence of the H^- band results in a smaller band-gap than in uncompressed pure H_2 , metallization is not an easy feat. For elemental Na, the $2p$ cores start to overlap with increasing pressure and the valence electrons are pushed into the interstitial regions [17], so that compressed Na is an insulator [18]. Already at 100 GPa the width of the Na $2p$ bands in the sodium polyhydrides is indicative of core overlap. As the pressure is tripled (up to 300 GPa), the bandwidth increases from 0.7-2.2 eV, 0.4-1.5 eV, and 0.3-1.4 eV for NaH_7 , NaH_9 and NaH_{11} . Cc - NaH_7 remains insulating up to at least 300 GPa (a $C2/m$ system with H^- atoms which is a semimetal at 100 GPa, but has a lower enthalpy than the Cc phase above 250 GPa was also found), and $P1$ - NaH_{11} becomes a semimetal at ~ 250 GPa.

The only structure which is thermodynamically stable and metallic is $Cmc2_1$ - NaH_9 . The band gap closes at ~ 200 GPa in our PBE calculations, and the enthalpy of this system becomes lower than that of the insulating Pm - NaH_9 phase at ~ 250 GPa. Within this pressure range the two phases — with distinct electronic structures — are within dynamic enthalpies of each other. In order to verify the metallicity of this phase, we have calculated the DOS using the HSE06 hybrid functional which is known to give good accuracy for band gaps [19]. Computations show that at 300 GPa $Cmc2_1$ - NaH_9 has a small but finite DOS at E_F (see the SI), indicating that metallization may occur near the pressure at which this structure becomes stable.

The primitive unit cell of $Cmc2_1$ - NaH_9 contains two formula units. Of the 18 H atoms two are hydridic—the closest Na atom is 1.72 Å away, and another three are found at 1.86 Å (the Na-H distance in $Pm\bar{3}m$ NaH at 300 GPa is 1.70 Å). Four of the H_2 units are slightly elongated, with Na-H distances of 1.65 and 2.27 Å. In the other four the H-H bond is somewhat shorter, and the distance to the nearest Na is roughly the same for both H atoms (1.65 and 1.79 Å).

The overlap of the Na cores in $Cmc2_1$ - NaH_9 at 300 GPa gives rise to a $2p$ bandwidth of 1.5 eV and a small density of states at the Fermi level ($g(E_F) =$

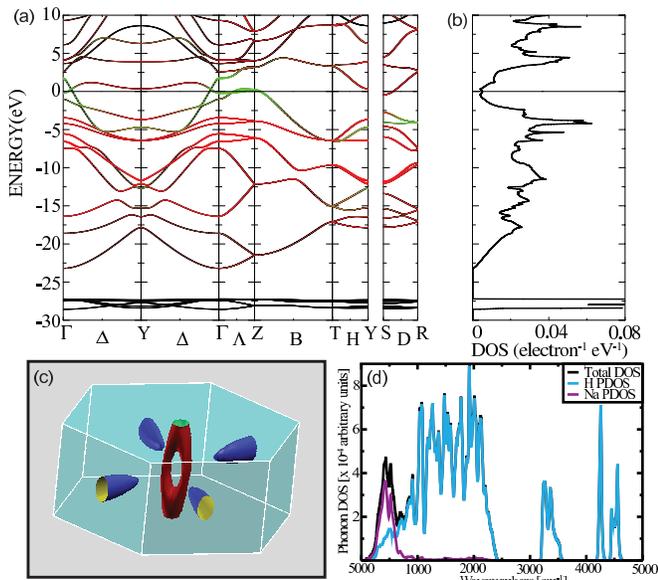


FIG. 3: (color online) (a) Band structure of $Cmc2_1$ - NaH_9 at 300 GPa, with $E_F = 0$. The width of the red/green bands is proportional to the s -character of the H_2/H^- hydrogens. The corresponding (b) density of states (DOS), (c) Fermi surface, and (d) phonon DOS. The total DOS, partial Na DOS and partial H DOS are given in black, purple and blue.

$0.01 \text{ eV}^{-1}/(\text{valence electron})$), see Fig. 3(a, b). Three distinct bands — two flat, and one steep — are metallic. It has been proposed that the simultaneous occurrence of bands with a small Fermi velocity (flat), and those with a large dispersion (steep) around E_F are necessary for superconductivity [20].

The fatness of the red/green bands in Fig. 3(a) is proportional to the s -character of the H_2/H^- hydrogens. The bands near the Fermi level can be attributed primarily to H^- . Two of the metallic bands, crossing E_F between $\Gamma - Y$ and $\Gamma - Z$ in the band structure, exhibit primarily H^- character. One of them gives rise to the long red ladder-type Fermi surface which stretches along the z -axis of the Brillouin zone, and the other to a green pocket embedded in the neck (Fig. 3(c)). The band crossing E_F between the S and R points (blue/yellow pocket in the Fermi surface) exhibits $H_2 \sigma^*$ -character.

The H-H distance of an H_2 molecule in the gas phase and in the solid at normal pressures is computed as being 0.75 \AA . Half of the H_2 units in $Cmc2_1$ - NaH_9 at 300 GPa have a slightly longer bond length of 0.80 \AA , in the other half the H-H distance is somewhat shorter (0.72 - 0.73 \AA). The former give rise to a peak in the phonon DOS (Fig. 3(d)) which is found at a lower frequency than that of a free H_2 vibron ($4,161 \text{ cm}^{-1}$) [21], and the latter to two distinct peaks at higher frequencies. The highest phonon frequency of $4,625 \text{ cm}^{-1}$ corresponds to an estimated Debye temperature of 6650 K , and the bands are

23 eV wide resulting in a reduced electron-electron repulsion. Despite the relatively low $g(E_F)$ NaH_9 may be a hydrogen-rich superconductor at pressures lower than those necessary to metallize pure hydrogen.

The tie-line in Fig. 1 illustrates that the NaH_n phases with an even number of hydrogen atoms are thermodynamically unstable with respect to decomposition into structures with where n is odd. For example, at 50 GPa the reactions $[NaH_8 + \frac{1}{6}NaH \rightarrow \frac{7}{6}NaH_7]$, $[NaH_8 + \frac{1}{2}H_2 \rightarrow NaH_9]$, and $[NaH_8 + \frac{3}{2}H_2 \rightarrow NaH_{11}]$ are predicted to be exothermic by 38, 83 and 153 meV, respectively.

A closer look at these even sodium high-hydrides (details given in the SI) is warranted since some of them may possess kinetic stability. Of particular interest are the metallic phases which were found to contain only H_2 units with slightly stretched bonds. These structures are similar to LiH_6 , and their metallicity is a result of the partial filling of the $H_2 \sigma_u^*$ bands by the Na $3s$ electrons.

$Pm\bar{3}m$ - NaH_6 becomes stable with respect to an insulating $P1$ phase above 150 GPa. The DOS calculated with the HSE06 functional at 200 GPa is very similar to the one obtained with PBE around the Fermi level (see the SI). This structure can be derived from the one found for LiH_6 , $R\bar{3}m$, by setting all of the rhombohedral angles to 90° . As expected, it is already metallic at 1 atm, though it is not stable. Upon further compression the Na $2p$ bandwidth increases substantially, with a concomitant decrease in $g(E_F)$. Nonetheless, NaH_6 remains metallic up to at least 300 GPa.

The enthalpy of metallic $Cmcm$ - NaH_8 becomes lower than that of an insulating $P1$ structure at ~ 200 GPa. As shown in the SI, it contains a unique extended network of H atoms. The unit cell cannot easily be derived from the most stable $I422$ - LiH_8 phase. Due to the increased fraction of hydrogen, the sodium cores overlap to a lesser extent than in NaH_6 , giving rise to a larger $g(E_F)$. Interestingly, despite the fact that at 300 GPa the Na $2p$ bandwidth is about 0.25 eV greater than that of NaH_9 , the system is a good metal with $g(E_F) = 0.033 \text{ eV}^{-1}/(\text{valence electron})$. This finding suggests that core overlap is more effective at preventing band gap closure in an insulating system, than it is at reducing the DOS at E_F of an already metallic phase.

NaH_{10} was also found to have two distinct structures, one stable between 50-150 GPa, and the other up to at least 300 GPa. Both of these contained only H_2 units, and both were good metals.

Phonon computations for NaH_6 , NaH_8 and NaH_{10} at 200, 200, and 50 GPa, respectively, did not reveal any imaginary frequencies confirming that these structures are minima. $Immm$ - NaH_{10} is particularly interesting, as it becomes stable with respect to NaH and H_2 at around 50 GPa with a high $g(E_F)$ ($0.030 \text{ eV}^{-1}/(\text{valence electron})$), and a substantial Debye temperature of $5,700 \text{ K}$. It is beyond the scope of this work to compute the barrier of decomposition of NaH_{10} into NaH_9 and $\frac{1}{2}H_2$. Provided

this structure is kinetically stable, it may be a superconductor at experimentally achievable pressures.

In conclusion, whereas at normal conditions a one-to-one NaH stoichiometry is the only one known, at experimentally attainable pressures the NaH₉ ratio is found to be stable. Perhaps even more remarkable is the prediction that a mixture of NaH and H₂ may lead to the formation of metallic sodium-polyhydrides at pressures significantly less than those necessary to metallize the constituent parts. Because of the lower IP of the heavier alkali metal, the NaH_{*n*} phases become stable at about 25 GPa, a fourth of the pressure necessary to stabilize LiH_{*n*}. As a result of the larger ionic radius of Na, the preferred *n* is found to be 1.5 times larger than the optimal *m*, suggesting that the heavier MH_{*n*} may contain an even higher mole percent ratio of the lightest element. Overlap of the Na 2*p* cores deters the metallization of the NaH_{*n*} with an odd number of hydrogen atoms, whose unit cells contain both H⁻, and H₂ units. Even though core overlap results in a decrease of the DOS at *E_F* of the even NaH_{*n*} systems containing only H₂ units (metallic because of population of the H₂ σ_{*u*}^{*} bands), these phases remain good metals until at least 300 GPa. We are looking forward to experimental and theoretical studies on these and heavier alkali polyhydrides which are likely to become stable at even lower pressures.

Finally we note that Li(NH₃)₄ can be viewed as an expanded alkali metal — a superatom where the valence electron density is pulled out to a greater extent than in the heaviest alkali metal, and whose IP is even lower [22]. This suggests that the search for superconductivity in [Li(NH₃)₄]_{*n*} and related systems may also bear fruit.

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- [10] Calculations were performed with the VASP 4.6 and 5.2 codes, [23], along with the PBE functional [24], an energy cut-off of 1000 eV, and plane-wave basis sets within the PAW method [25]. For Na the 2*s*, 2*p*, 3*s* electrons were treated explicitly, and for H a hard all electron PAW was used. The *k*-point grids were generated using the Γ -centered Monkhorst-Pack scheme, and the number of divisions along each reciprocal lattice vector was chosen so that the product of this number with the real lattice constant was 50 Å. The DOS (which agreed well with the one obtained by VASP), band structure, and Fermi surface of NaH₉ in the text were obtained with HiLAPW [26]. In order to obtain more accurate metallization pressures, the DOS of *Pm* $\bar{3}m$ -NaH₆ at 200 GPa, and *Cmc*2₁-NaH₉ at 300 GPa was computed using the HSE06 [19] hybrid functional. For structural searches we used the open-source EA XtalOpt (<http://xtalopt.openmolecules.net/>), and the parameter set suggested in Ref. [9]. Tests on an 8 atom supercell of NaH verified that XtalOpt correctly predicts the crystal structures at *P* = 0 – 350 GPa. Exploratory runs on NaH_{*n*} showed that the most stable systems will have a higher mole percent ratio of hydrogen than the most stable LiH_{*n*} phases. Thus, we focussed on NaH_{*n*} with *n* = 6 – 12 where the unit cell contained up to 4 (NaH₆) and 2 (NaH₆-NaH₁₂) formula units. EA searches were carried out at 100 and 300 GPa, and the EA was stopped when either the same lowest enthalpy structure appeared at least five times, or the number of structures which had been optimized was greater than twenty times the number of atoms in the unit cell. ΔH_F were calculated with respect to NaH (*Fm* $\bar{3}m$, NaCl-structure from 0 to 30 GPa and *Pm* $\bar{3}m$, CsCl-structure from 40-300 GPa) and the H₂ structures from Ref. [8].
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