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Synthesis of Sodium Polyhydrides at High Pressures

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Abstract: The only known compound of sodium and hydrogen is archetypal ionic NaH. Application of high pressure is known to promote states with higher atomic coordination, but extensive searches for polyhydrides with unusual stoichiometry have only limited success in spite of several theoretical predictions. Here we report the first observation of formation of polyhydrides of Na (NaH₃ and NaH₇) above 40 GPa and 2000 K. We combine synchrotron x-ray diffraction and Raman spectroscopy in a laser heated diamond anvil cell and theoretical Ab-Initio Random Structure search, which both agree in stable structures and compositions. Our results support the formation of multicenter bonding in a material with unusual stoichiometry. These results are applicable to the design of new energetic solids and high-temperature superconductors based on hydrogen-rich materials.

Introduction.

Dense hydrogen is of central interest in many disciplines, especially in high-pressure science. It is expected to possess unusual properties such as high energy density (1), high-temperature superconductivity, and superfluidity (2). Unusual high-pressure properties may be sustained at ambient conditions, if a predicted metastable metallic phase of hydrogen (3) could exist at ambient pressure. This phase would have unusual anisotropic structure, consisting of weakly interacting chains of hydrogen atoms with interatomic distances about 1.06 Å (3). Looking for another route to force hydrogen into a metallic state, Ashcroft (4) proposed that such conducting states could be realized in hydrogen-rich alloys, where hydrogen is in a “pre-compressed” or otherwise altered electronic states induced by the host material (“dopant”) in such a way, that the electronic bands of hydrogen and the host element(s) overlap at the Fermi level. For example, metallic polyhydrides of lithium have been proposed (5, 6) to exist at pressures about 100 GPa, well below the expected metallization pressure of pure hydrogen (7). It should be noted that in lithium polyhydrides the metallization does not occur due to “precompression” of hydrogen molecules, but rather due to “doping” by electropositive element (5, 6). Stable polyhydrides of alkali and alkaline earth metals have been predicted recently by theoretical analysis of MH_n ($M= Li, Na, K, Rb, Cs, Sr$) compounds with variable hydrogen composition (5, 6, 8-13).

The compounds with $n \geq 2$ are expected to become stable at pressures as low as 25 GPa in the case of Na and above 100 GPa in the case of Li. New polyhydride phases are also anticipated for alkaline earth metals (10, 14, 15). The theoretically predicted polyhydrides are not only stabilized by compression, but are also expected to metalize and exhibit superconducting properties at lower pressures than the constituent parts--the conventional hydride and hydrogen. For example, critical superconducting temperatures as high as 235 K have been predicted for polyhydrides of Ca (14). Moreover, recent discovery of superconductivity in hydrogen sulfide at record $T_c \sim 200$ K at high pressure (200 GPa) has confirmed great potential of dense hydride materials as high-temperature superconductors (16). These compounds provide new chemical means to alter the electronic structure, facilitating the creation of metallic superconducting hydrides with record high critical superconducting temperatures. Notably, linear H_3^- ions were predicted

to form in polyhydrides of softer alkali metals, for example in RbH_5 (18) and CsH_3 (11). Such H_3^- ions have a tendency to be stabilized in a linear configuration, contrary to triangular-shaped H_3^+ ions (19, 20). It should be noted here, that almost perfectly triangular ions H_3^+ were predicted to be stable in the crystalline structure of H_5Cl (21) at high pressures up to 300 GPa. Symmetric H_3^- ions with interatomic distance 1.06 Å and with the lowest potential barrier (22) were discussed as transition states in hydrogen exchange processes of metal complexes (23). H_3^- and D_3^- ions were experimentally observed in discharge plasmas only recently (24). The chains of H_3^- ions that were predicted theoretically in RbH_5 (11) and CsH_3 (18), resemble one-dimensional hydrogen chains of ambient pressure metastable metallic hydrogen phases predicted in 1972 by Browman and Kagan (3). Such chains were also extensively discussed as the simplest model of strong correlations in a linear chain of hydrogen atoms (25, 26).

Despite a wealth of theoretically predicted high pressure polyhydride structures, none of the predictions has been confirmed until now, except possible Li polyhydride phases. The polyhydrides of Li were reported recently, based on the measurements of the infrared absorption spectra of LiH by Pepin et al (27). New absorption bands appearing above 130 GPa are consistent with calculations of the infrared modes in LiH_6 and LiH_2 . The new polyhydrides of Li have been produced by compression of LiH in a rhenium gasket without any pressure medium. Both compounds remain optically transparent to 215 GPa, which is at odds with calculations (28). The authors did not attempt to characterize their samples by x-ray diffraction method and Raman spectroscopy, making it difficult to estimate if they had significant amounts of the reacted materials in their high pressure samples.

Here we report synthesis of Na polyhydrides at pressure of about 30 GPa in laser heated diamond anvil cell (DAC) experiments at temperatures above 2000 K. We were guided by *ab-initio* theoretical search, which yielded a number of stable NaH_x ($x=1.5-13$) materials (Fig. 1) more favorable than those predicted previously (8). In agreement with these predictions, we identified the NaH_3 solid using *in-situ* synchrotron x-ray diffraction measurements. Moreover, both x-ray diffraction and Raman spectroscopy revealed the presence of the NaH_7 phase, which has a characteristic Raman band at 3200 cm^{-1} , suggesting the formation of H_3^- ions. Our results therefore provide the first verification of

the existence of polyhydrides of alkali metals with heterogeneous (multicenter) chemical bonding and prospects for lower pressure metallization. These new materials provide chemical route to dense hydrogen-based phases that have a potential of being high-temperature superconductors. The possibility of metastable phases should be carefully explored in the future studies, since the new polyhydrides may be implemented as hydrogen storage materials with hitherto unexplored physical and chemical properties.

Results

X-ray diffraction experiments and Raman measurements.

Several experiments were performed with Li and Na samples up to 70 GPa at room temperature. In these runs, only formation of LiH and NaH was detected, with no indication of polyhydride phases. The results of these experiments were similar to previously reported attempts (29), however, we were able to identify Li and Na metals up to 35 GPa, and 50 GPa, respectively, without complete transformation to the monohydride form. To overcome possible kinetic barriers to the formation of polyhydrides, we performed laser-heating experiments on these samples. For Li in hydrogen we were able to perform a few experiments above 50 GPa with laser heating up to 1900-2000 K, in which only the monohydride of Li (LiH) was formed. We were not able to detect any polyhydrides of Li under these conditions. Similar measurements for Na in hydrogen at 32 GPa yielded a significant enhancement of the XRD signal from NaH. Further heating of Na and NaH in H₂ - saturated environment to ~ 2100 K produced a laser flash that resulted in sample changes (runaway material forming a ring centered at the flash position – see inset in Fig. 3), indicating the onset of chemical reactions. The Raman spectra collected from temperature quenched sample within reacted area showed the formation of a new material with two additional vibron peaks around 4000 cm⁻¹, one of them softer than the pure H₂ vibron, and another one harder (Fig. 2). However, we were unable to detect a reliable XRD signal from the very tiny sample reaction area. We repeated the laser heating experiment with a NaH sample loaded in the DAC with H₂ and Au fragments for measuring pressure and for better coupling to the laser during heating. This experiment produced large amounts of a new phase after laser heating at 30 GPa. As the temperature was increased above 2100 K the heating conditions ran away and resulted in a very bright flash (avalanche) saturating the detector. From the brightness of

the heating spot, we estimated the temperature to be in the range of 4000-6000 K. We did not attempt to repeat heating due to the risk of breaking the diamonds but saved the sample for further characterization. After heating we could clearly see the change in the sample shape, indicating the sample transport within the laser-heated reaction area of around 20 μm in diameter.

The newly synthesized phases were characterized by XRD and Raman measurements in the pressure range from 18 to 50 GPa. Decompression of the DAC below 18 GPa resulted in decomposition of the newly formed phase, which was confirmed by the disappearance of their characteristic Raman signatures. These experiments are very challenging since the presence of hydrogen under high pressure-temperature conditions often leads to diamond breakage. Most of the experiments resulted in failure of the diamond during laser heating; however, we succeeded in producing Na polyhydrides in two runs out of ten, and characterized them using Raman spectroscopy and XRD. The experimental results are described below. Before describing these results, we summarize below our theoretical findings, which differ in a number of aspects from the previous theoretical study of Baettig *et al.* (8). These differences are crucial for understanding our experimental results.

Theoretical calculations of sodium polyhydride structures.

We searched for low enthalpy structures using a variety of compositions of Na-H at 50 GPa with the *Ab-Initio* Random Structure Searching (AIRSS) method (6), which has previously been applied to hydrides under pressure(30),(6). The calculations used density functional theory (31), (32) and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof for the exchange-correlation functional (33), (34). AIRSS was conducted at 50 GPa with the CASTEP plane wave code (35) and ultrasoft pseudopotentials (36). Further details are provided in Methods section.

We performed calculations for the structures reported by Baettig *et al.* (8) and successfully reproduced their data for NaH₇, NaH₉, and NaH₁₁. We used AIRSS to study other compositions and we found the NaH₃ phase. This prompted us to extend our searches to lower hydrogen compositions such as NaH₂, Na₃H₅, and Na₂H₃. For most compositions, we studied simulation cells containing 1, 2, and 4 formula units (f. u.), and

for NaH_2 and NaH_3 , we conducted AIRSS on up to 6 f. u. The most stable materials found consisted of H_2 and NaH structural units. This finding lead us to generalize the form of the stable composition to $(\text{NaH})_m(\text{H}_2)_n$ (Fig. 1). We studied (m,n) pairs ranging from (4,1) to (1,6). We also tested other compositions such as Na_2H_5 , Na_2H_7 , and Na_2H_9 , but we found them unstable with respect to decomposition into nearby stable compositions, as shown in Fig.1 (a). Previous theoretical work suggested that NaH_n ($n > 6$) can be stabilized above 50 GPa (8). As shown in the convex hull diagram of Fig. 1 at 50 GPa, generally, many combinations of (NaH) and H_2 can be stabilized. The Na_2H_3 , Na_3H_5 , NaH_3 , NaH_9 , and NaH_{13} phases (shown in blue) lie on the convex hull at 50 GPa. In addition, although they are not thermodynamically stable, NaH_2 , NaH_5 , NaH_7 , and NaH_{11} (shown in green) are dynamically stable as demonstrated by the phonon dispersion data (phonon and electron DOS are shown in Supplementary Methods from Supplementary Fig. 3 to Fig. 29) and in the paper of Baettig *et al.* (8).

The enthalpy differences between the thermodynamically stable phases (blue line) and the dynamically stable phases (green) are only about 10 meV/atom. We also calculated the nuclear zero point energy (ZPE) within the harmonic approximation to estimate the effects of vibrations on the total enthalpy. We found a monotonic increase in the ZPE with the fraction of H atoms in the various hydrides, ranging from 150 meV / atom in NaH to ~ 240 meV / atom in H_2 (Supplementary Materials, Fig. 31).

In figure 1 (a), NaH_7 is not thermodynamically stable but in our calculations including ZPE effect (figure 1 (b)), we found that NaH_7 comes within 1~2 meV / atom of being thermodynamically stable. The stability of NaH_7 relative to other stable phases increases with temperature, and in figure 1 (c), we show that NaH_7 becomes eventually a thermodynamically stable phase at 300 K. The temperature corrections for different polyhydride phases are summarized in Supplementary Materials Fig. 31.

Analysis of synthesized sodium polyhydride phases.

The Raman spectra of the NaH_n materials synthesized by laser heating (Fig. 2) show a number of features, which are distinct from those of the pure hydrogen within the same sample chamber under the same pressure (50 GPa). New modes at 4100 cm^{-1} and 4200 cm^{-1} , bracketing the H_2 vibron at 4160 cm^{-1} , point to the formation of a new phase

containing H₂ molecules embedded within the sodium polyhydride crystal structure. Moreover, as shown in Fig. 2, another set of Raman modes appears around 3200 cm⁻¹, suggesting a strongly modified H₂ species, possibly similar to the predicted H₃⁻ species or molecules in polyhydrides of Cs (11) or K (9). Similar or even lower Raman frequencies are characteristic of dihydrogen moieties observed in transition metal complexes (37),(38) and other chemical environments (39). The low frequency region of the Raman spectra (Supplementary Materials, Fig. 1) also suggests a structure very different from pure hydrogen (e.g.(40)) and the initial body centered cubic (bcc) NaH monohydride, which is not expected to have any allowed first order Raman active modes. Indeed, our Raman measurements for unreacted sample regions in the DAC did not produce any Raman signatures of NaH, but indicated the presence of pure solid H₂ judging from its characteristic vibron and roton bands. The low-frequency Raman spectrum of the newly synthesized material consists of strongly pressure-dependent bands at 200-800 cm⁻¹, which we identify as lattice modes in contrast to weakly pressure-dependent rotational modes of pure H₂. (Fig. 1 of the Supplementary Materials)

Figs. 3,4 show an XRD pattern of a new material at 40 GPa. XRD data were also obtained away from the reacted area at each pressure (see inset to Fig.3). Three different "families" of reflections from different phases were observed to coexist in the XRD patterns of the reacted area: i) the unreacted bcc NaH [ambient pressure face-centered cubic (fcc) NaH transforms to bcc at 29 GPa (41)], ii) the fcc Au used as a pressure marker and as laser absorber, and iii) the synthesized NaH_n. In order to fully identify the reflections from the synthesized NaH_n, we performed a detailed comparison of the XRD patterns on and away from the reacted area. A typical example is shown in Fig.3. The positions of all reflections attributed to NaH and Au, are in full agreement with the known EOS of bcc NaH (41) and fcc Au, implying the absence of chemical reaction between Au and H. The reflections of bcc NaH and Au have then been subtracted when performing the final structural refinement of the NaH_n phases (Supplementary Fig.2). This has been performed via a Rietveld refinement only for bcc NaH and fcc Au with a subsequent subtraction of the refined peaks from the raw patterns. After all reflections not belonging to the synthesized NaH_n have been successfully identified we compared the calculated XRD patterns of the predicted stable structures with the observed ones. Full

indexing-refinement of the observed reflections, without the use of the predicted phases as candidates, is very difficult for a variety of reasons. First, the XRD intensity depends almost exclusively on the positions of the Na atoms. Second, the large number of observed peaks suggests a low symmetry unit cell. Finally, the texture of the 2-D images of the XRD data suggests a mixture of phases. Based on this analysis, we find that NaH₃ is the predominant phase of the synthesized material (Fig. 4). Indeed, all the main reflections can be indexed with the orthorhombic *Cmcm* NaH₃ cell. Moreover, the experimentally determined lattice parameters and cell volume (at 40 GPa: $a=3.332 \text{ \AA}$, $b=6.354 \text{ \AA}$ and $c=4.142 \text{ \AA}$ with $V_{\text{pfu}}=21.93 \text{ \AA}^3$) of NaH₃ are in full agreement with the theoretical predictions (Fig. 4). However, there are a few reflections that cannot be indexed with the NaH₃ cell. For hydrogen contents lower than in NaH₅, the phonon density of states has two well-separated bands, below 1500 cm^{-1} for Na-H interactions and around 4000 cm^{-1} for H₂ vibrations. At higher hydrogen concentrations, we found the formation of other intermediate frequency bands near 3200 cm^{-1} . Having in mind that NaH_n phases ($n < 7$) cannot support the existence of Raman modes at 3200 cm^{-1} (Supplementary materials) we have to include phases with $n > 6$ (7, 9) in our analysis. From the various phases only the monoclinic *Cc* NaH₇ phase shows reasonable agreement with the observed patterns. Indeed, some of the main observed reflections can only be indexed with the NaH₇ phase with experimental lattice parameters $a=6.99 \text{ \AA}$, $b=3.597 \text{ \AA}$, $c=5.541 \text{ \AA}$ and $\beta=69.465^\circ$ (theoretical values $a=6.732 \text{ \AA}$, $b=3.643 \text{ \AA}$, $c=5.577 \text{ \AA}$ and $\beta=69.36^\circ$) at 40 GPa. With the use of both phases, NaH₃ and NaH₇, we have successfully indexed all observed reflections of the synthesized mixed-NaH_n material (Fig. 4). We summarized experimental and theoretical lattice parameters and volume as a function of pressure in Fig.5. Notably, while experimental volumes of NaH₃ and NaH+H₂ are very close, the volume of NaH₇ is significantly lower than the volume of components NaH+3H₂. The PV term of NaH₃ is practically the same (given the experimental error in both the reported EOS of NaH and H₂) with that of NaH+H₂. There is a very good agreement between observed and theoretically predicted relative intensities of Bragg reflections. However, a refinement of the positional parameters was not possible due to the "spotty" XRD rings. Finally, Fig.6 provides some details of electronic structure of new phases as follows from the theoretical analysis. The electronic density of states is

compatible with insulating phase for both materials, with a reduced band gap being slightly larger than 2 eV as follows from the standard DFT calculation. It is well known that standard DFT method underestimates the band gaps of most semiconductors and thus it is expected that the real band gap in NaH₃ and NaH₇ could be larger than calculated one. For NaH₃ we calculated metallization pressure about 250 GPa, similar to metallization pressures predicted for higher polyhydrides in Ref. (8). For NaH₇ we found that electronic density contours clearly indicate formation of H₃⁻ units – Fig.6 (c), (d).

Discussion

The Raman and XRD data point to the formation of Na polyhydrides in the predicted stability range (above 20 GPa). While we were unable to isolate a single well-defined polyhydride phase, the data analysis strongly supports existence of several phases (NaH₃ and NaH₇, and possibly higher polyhydrides) in the reacted sample. Most of the theoretically predicted stable Na polyhydride phases have low symmetry structures, which are extremely difficult to characterize by XRD from the small samples available in the laser-heated region. While prolonged laser heating at well-defined *P-T* conditions may be beneficial for growing a single-phase sample, such experiments are still inaccessible due to the high reactivity of hot hydrogen with diamond anvils. Notably, Raman spectroscopy provided a more sensitive tool than XRD for characterizing formation of small amounts of low-Z polyhydride materials. Based on the results of theoretical calculations, we found that the Raman bands observed experimentally near 3200 cm⁻¹ can be assigned to an extended hydrogen molecular H₂ unit with an intramolecular length *d* of ~ 0.82 Å. This H₂ molecule is linked to a hydrogen atom in the NaH unit with a distance of *z*= 1.25 Å by sharing valence electrons (Fig. 6 c and d), and they form a H₃⁻ linear anion in NaH_{*x*} materials with *x*=7 (Figs. 2 and 6). It was suggested that pressure can induce a linear geometry for H₃⁻, which has four electrons, but a triangular geometry for H₃⁺, which has two electrons (20); recent confirmation of these simple chemical arguments was provided by a careful theoretical study of heavy alkali-metal hydrides under pressure predicted to form linear H₃⁻ in KH₅. To gain further insights into H₃⁻ anion formation in NaH₇, we analyzed the charge density of NaH₃ and NaH₇ using Bader analysis (Fig.6). The calculations confirmed the highly ionic nature of the NaH unit in each polyhydride: the net charges on Na and H in the NaH

unit are +0.79/+0.82 and -0.65/-0.47 in NaH₃/NaH₇, respectively, indicating that a significant portion of the electron density is donated to the H₂ molecules in NaH₇. In fact, the H₃⁻ anion in NaH₇ has an excess of -0.63 electrons and accordingly, H₂ in H₃⁻ anion possesses -0.16 e, which leads to the elongation of the H₂ bond.

Ab-initio phonon calculations give information on the dynamical stability of the phases. The stability region of NaH₇ was predicted (8) to be 25-100 GPa which is consistent with our experiments. All lattice and vibron modes of the polyhydrides increase monotonically in frequency with pressure up to 50 GPa. Our theoretical calculations show dynamical stability and structural stability of predicted phases, including NaH₃ and NaH₇.

In summary, we synthesized polyhydrides of Na in a laser-heated DAC at pressures above 30 GPa and temperatures above 2000 K. We also performed detailed theoretical studies and found new stable phases of Na polyhydrides. One of these phases, NaH₃, matches well the XRD patterns collected from the reacted region. However, the x-ray patterns also suggest the existence of higher polyhydrides (NaH_n, n≥7), which is supported by the analysis of the Raman spectra in the 3200 cm⁻¹ region. Notably, higher polyhydrides of sodium appear to stabilize H₃⁻ unit predicted for other, heavier alkali metals (18). Polyhydrides of alkali metals open a new class of materials with pressure-stabilized multicenter (3 center – 4 electron) bonds for future investigation. Polyhydrides may provide chemical means to pre-compress hydrogen and provide a route facilitating the creation of metallic superconducting hydrogen compounds at reduced pressures. The possibility of metastable phases should be carefully explored in the future studies, since the new polyhydrides may be implemented as hydrogen storage materials with hitherto unexplored physical and chemical properties.

Methods

High-pressure experiments.

We have studied the formation of Li and Na polyhydrides in a DAC at pressures up to 70 GPa with laser heating to 2000 K and higher temperatures. The experiments were performed in a symmetric DAC (42). The samples of Li, Na, LiH, and NaH were loaded, along with small fragments of Au, in a glove box with controlled atmosphere (less than 1 ppm of oxygen). According to recent experimental (43) and theoretical (44) results, no

chemical reaction is expected between Au and H₂, up to the highest pressure of this study. Each sample was sealed in a DAC inside a glove box, and transferred to a gas-loading apparatus, where a H₂ pressure of about 200 MPa was created. The DAC was opened under the H₂ pressure to let the gas in, resealed, and then taken out for further high-pressure experiments.

X-ray diffraction (XRD) measurements and on-line laser heating were performed at the Sector 13 (GSECARS), Advanced Photon Source at the Argonne National Laboratory(45). The DAC was cooled below 200 K with nitrogen jet from Cryostream-type unit manufactured by Oxford Cryosystems.

Raman measurements were performed using off-line custom-made Raman system at GSECARS, the data were taken with Ar ion laser excitation (wavelength 514.5 nm).

Theoretical calculations.

In theoretical calculations, we used a plane-wave basis set cutoff energy of 1000 eV and a Brillouin-zone integration grid of spacing $2\pi \times 0.05 \text{ \AA}^{-1}$. Phonon calculations were performed with density functional perturbation theory using the Quantum Espresso code (46) with a kinetic energy cutoff of 70 Ry. The BZ integrations in the calculations were performed using Monkhorst-Pack meshes (47). We refer to meshes of k-points for electronic structure calculations and meshes of q-points for phonons. The phonon calculations used 24x24x24 k-points mesh and 8x8x8 q-points mesh for the most studied Na-H compounds and 12x12x12 k-points with 6x6x6 q-points mesh is used for relatively bigger unit cell compounds (Na₂H₃ and Na₃H₅).

References and Notes:

[±] The first two authors made equally important contributions in experiment (VVS) and theoretical analysis (DYK) to the presented work.

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Author Contributions:

V.V.S. has developed experiment conception and design, loaded the samples in DAC, performed acquisition of data, analysis and interpretation of data, wrote the article draft and revised critically for important intellectual content at all stages; DYK performed theoretical analysis, participated in writing the article draft and revised critically for important intellectual content; ES participated in data acquisition, analysed x-ray diffraction data, revised the paper critically for important intellectual content; TM loaded the samples in DAC, performed acquisition of data, revised the paper critically for important intellectual content; H.-K. Mao revised article draft critically for important intellectual content at all stages; CJP performed theoretical analysis, revised a paper draft critically for important intellectual content; RJN performed theoretical analysis, revised a paper draft critically for important intellectual content; VP developed experiment conception and design, helped in performing acquisition of data, analysis and interpretation of data, revised a paper draft critically for important intellectual content; AFG participated in acquisition of data, analysis and interpretation of data, edited article draft and revised critically for important intellectual content at all stages.

Competing Financial Interests

The authors declare no competing financial interests.

Figure legends

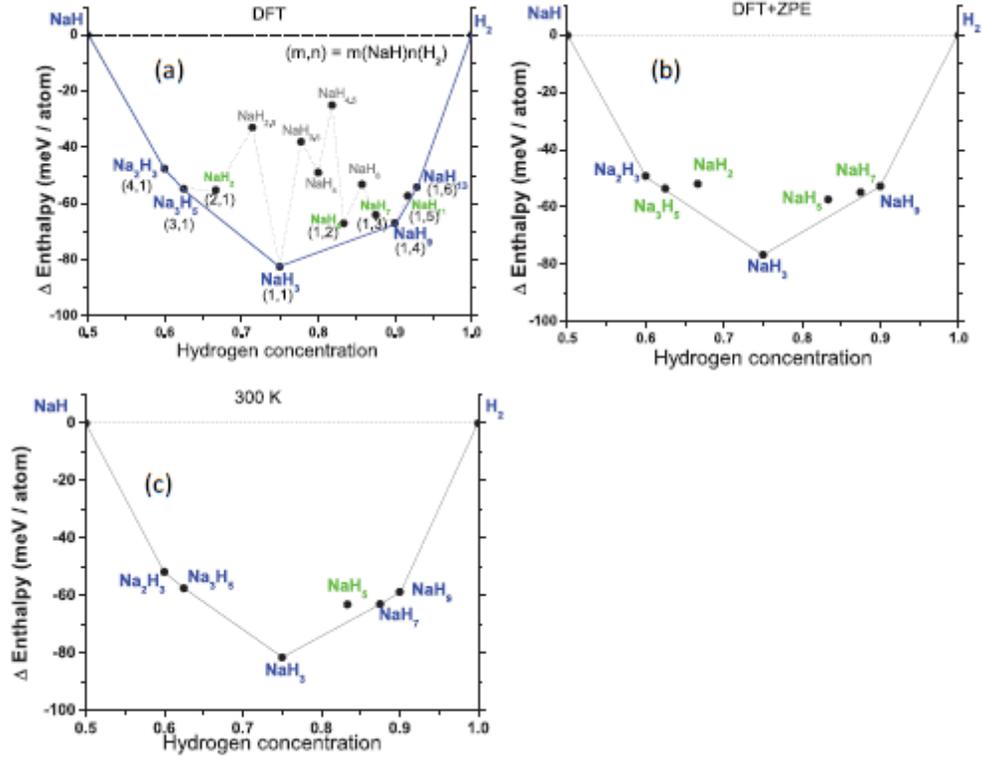


Fig. 1. Calculations of stable sodium polyhydride compounds. Convex hull curve of Na-H compounds at 50 GPa with respect to the decomposition (horizontal dashed line) into NaH and H₂ using (a) DFT (b) including ZPE, and (c) including temperature (300 K). Chemical formula in blue (green) shows predicted stable (meta-stable) compounds. The (m,n) correspond to compositions in units of NaH and H₂, respectively. Chemical formulas in black are found to be stable against the decomposition into NaH and H₂, however, they possess relatively high total energy compared to other stable (meta-stable) phases.

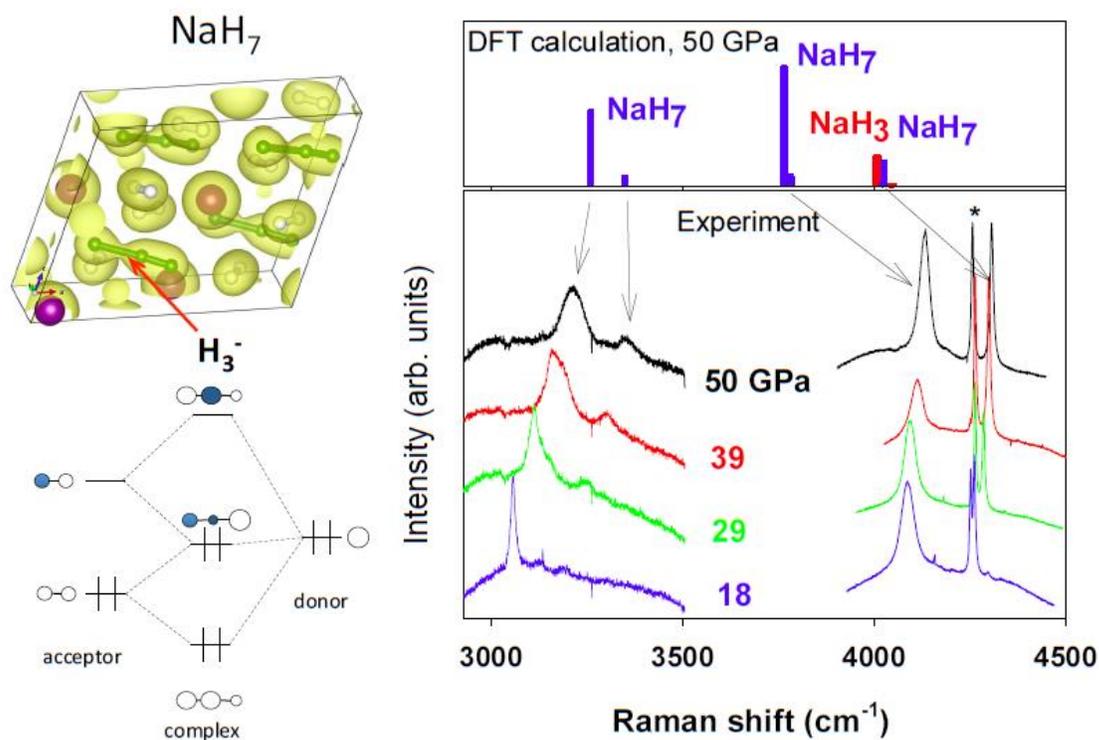


Fig. 2. H_3^- complexes responsible in NaH_7 and Raman spectra of NaH_n samples. The right panel shows higher-frequency vibrons from H_2 molecular-type structural units. The left panel shows the structure of NaH_7 , which contains H_3^- complexes. The isosurface is plotted at the level of $0.07 \text{ electrons}/\text{\AA}^{-3}$. One of H_2 molecules is bonded to a hydrogen atom in the NaH unit with a bonding length of $z=1.25 \text{ \AA}$, and they form a H_3^- linear anion in NaH_x materials with $x=7$. We presented detailed charge analysis below (Fig.6). The schematic diagram for H_3^- molecular orbitals (adopted from Ref. (48) for I_3^-) is also shown. Donor stands for hydride ion H^- , and acceptor for H_2 unit attached to H^- . Right panel: Raman spectra of NaH_7 sample are shown in the frequency region ($3000\text{-}3500 \text{ cm}^{-1}$) typical for vibrons from H_3^- units (indicated in the structure of NaH_7 as green-yellow dumbbells). The Raman response in $4000\text{-}4300 \text{ cm}^{-1}$ region is a mixture of NaH_3 and NaH_7 Raman modes. The top panel shows calculated Raman Intensity for NaH_3 and NaH_7 . Raman signal from a pure H_2 vibron is indicated by an asterisk.

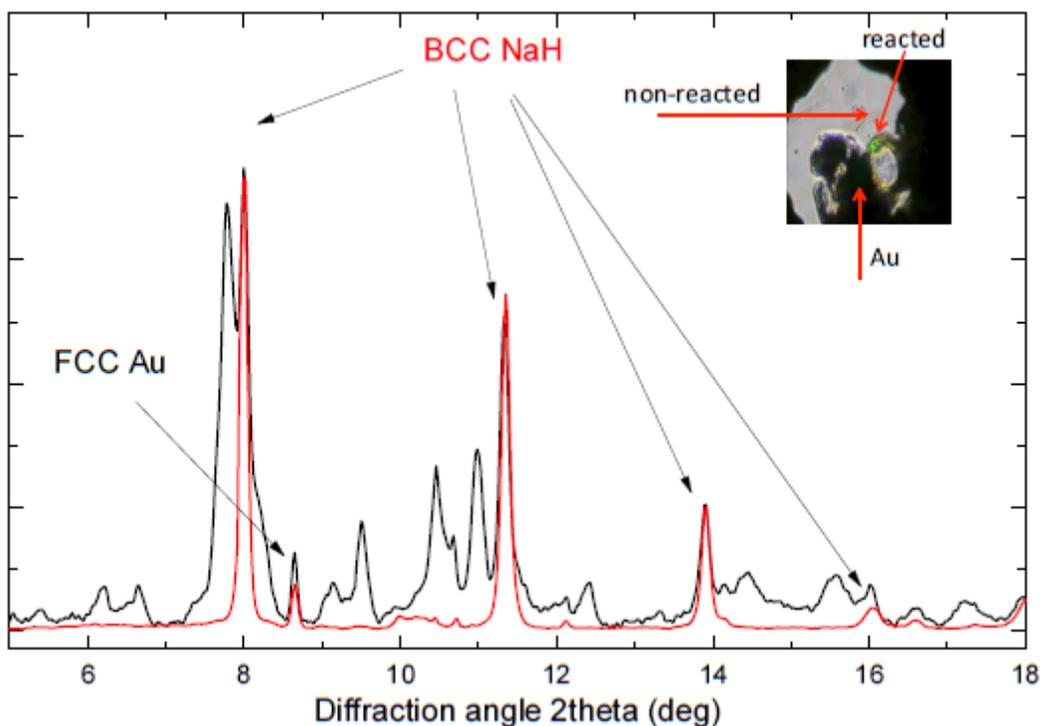


Fig.3. Structural information from x-ray diffraction measurements. XRD raw pattern (black) of the reacted area of the sample at 50 GPa, containing Bragg peaks from BCC NaH and FCC Au, which are indicated by arrows. The red XRD pattern is from a non-reacted area of the sample containing only BCC NaH and FCC Au. The perfect match of the position of the NaH peaks between the reacted and the non-reacted area justifies our argument about the origin of these peaks. Inset shows a reacted sample, dark sample in a gasket hole is Au+Na, transparent part is NaH+H₂, the smaller dark circle with a green laser spot is a reacted area. The darker color of the reacted area is compatible with a reduced bandgap (~2 eV) resulting from calculations (Fig.6).

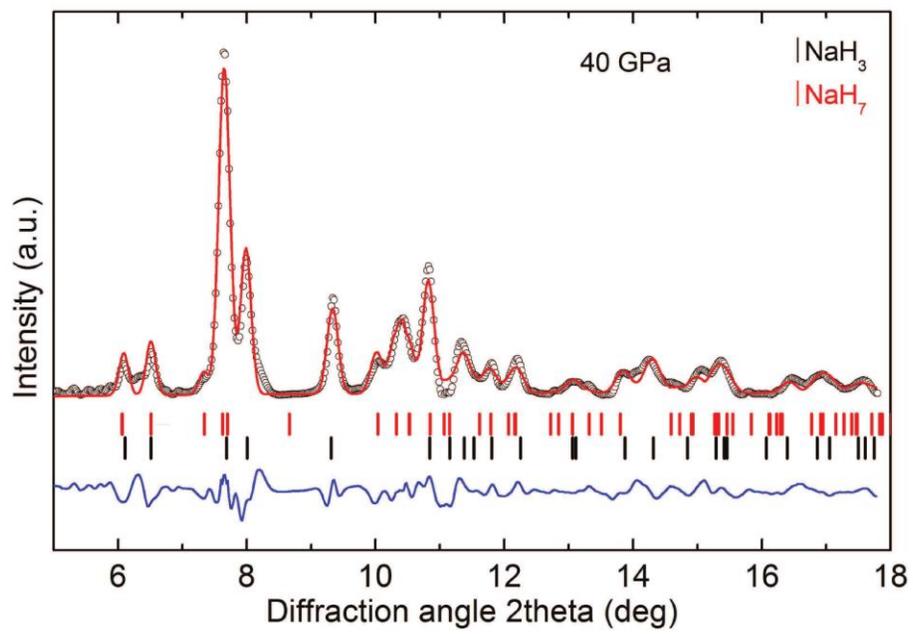


Fig. 4. Le Bail refinement for NaHn at 40 GPa. NaH₃ and NaH₇ peaks are marked with black and red vertical lines respectively.

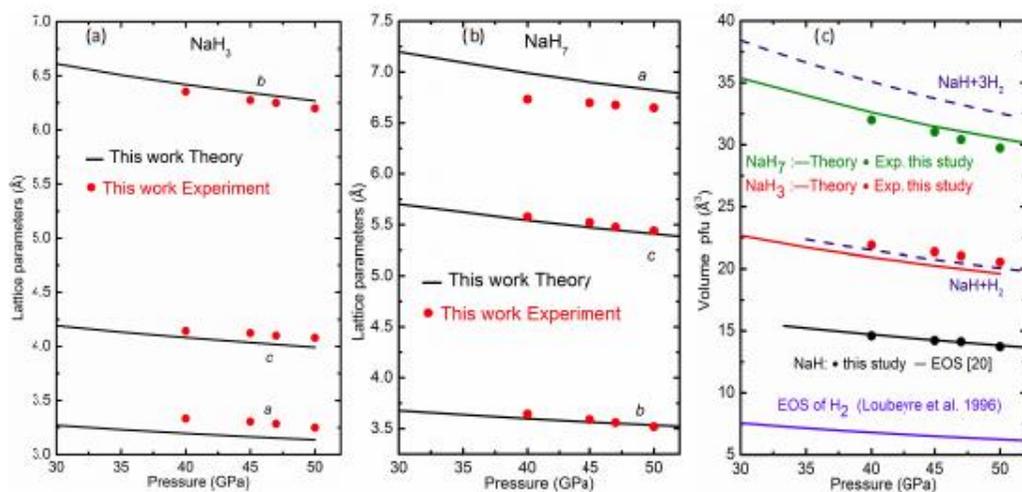


Fig. 5. Lattice parameters and equations of state of NaH₃ and NaH₇.

(a) Lattice parameters of NaH₃ as function of pressure.

(b) Lattice parameters of NaH₇ as function of pressure. (c) Equations of state (EOS) of

NaH₃, NaH₇ in comparison with EOS of NaH and H₂. Experimental data: red and black circles, theoretical predictions: green, red, and black continuous lines (specified in the figure). EOS of H₂ is also shown (blue line).

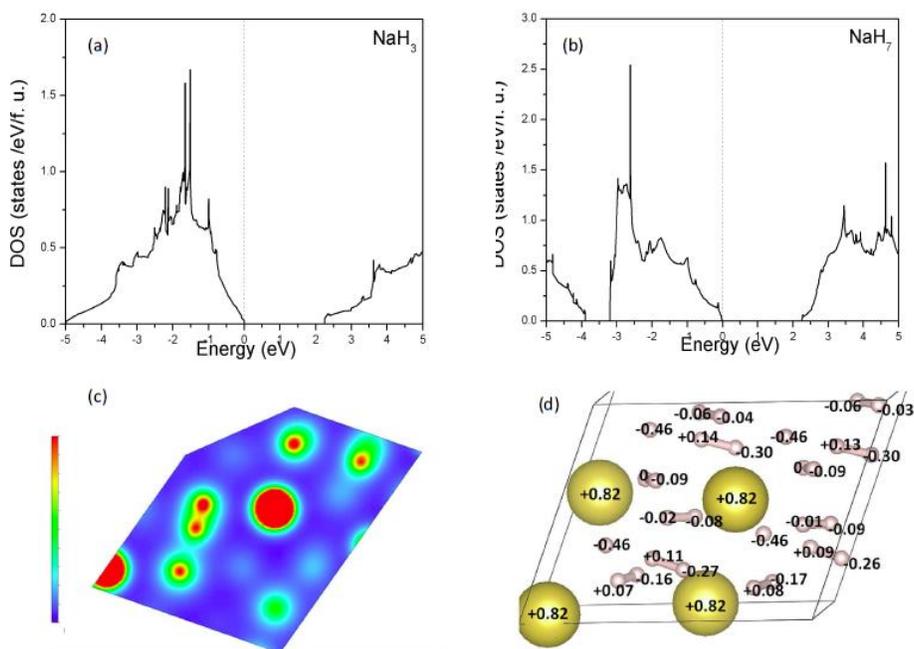


Fig. 6. Calculated electronic properties of NaH_3 and NaH_7 at 50 GPa.

Density of electronic states of NaH_3 (a) and NaH_7 (b). (c) A contour plot of H_3^- unit in NaH_7 . This image shows a charge density contour with a saturation level of 0.3 electrons \AA^{-3} (which is much higher than 0.07 of the iso-surface plot in Fig.2). An equi-charge density level of H_3^- unit is evident from the plot, which was prepared for the Miller indices (1 2 -1). (d) Bader analysis showing excessive charge of individual atoms in NaH_7 . Na cations have a charge +0.82 and ionic linked hydride H has a charge of -0.46. H_2 molecules with higher vibron frequencies have less polarized charges (they form pairs with charges -0.06 & -0.04, -0.06 & -0.03, 0 & -0.09, -0.02 & -0.08, +0.07 & -0.16). However, the H_2 molecules which are linked to the hydride ion H(-0.46) are highly polarized (+0.14 & -0.30, +0.13 & -0.30, +0.11 & -0.27, +0.09 & -0.26).