Metallization of hydrogen by the fcc lattice intercalated with ammonium ions at low pressure

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Abstract

Metallic hydrogen is capable of room temperature superconductivity, but its experimental synthesis conditions are extremely hard. Therefore, it is a good choice to reduce the synthesis pressure of metallic hydrogen by adding other chemical elements. However, for most hydrides, the metallization of hydrogen by "chemical precompression" to achieve high-temperature superconductivity still requires relative high pressure, which makes experimental synthesis difficult. How to achieve high-temperature superconductivity in the low-pressure range (⩽50 GPa) is a key issue for realizing practical applications of superconducting materials. Toward this end, this work proposes a strategy for the insertion of ammonium ions in the fcc crystal. High-throughput calculations of the periodic table reveal 12 elements that are kinetically stable and superconducting at low pressures, where the highest superconducting transition temperatures of AlN$_2$H$_8$, MgN$_2$H$_8$ and GaN$_2$H$_8$ can reach up to 118.40, 105.09 and 104.39 K. Pressure-induced bond length changes and charge transfer reveal the physical mechanism of high-temperature superconductivity, where the H atom continuously gains electrons leading to the transition of H$^+$ ions to atomic H, which achieves metallic hydrogen under mild pressure. Our results also reveal two strong linear scalar relationships, one is the H-atom charge versus superconducting transition temperature and the other is the first ionization energy versus the highest superconducting transition temperature. Besides, ZnN$_2$H$_8$, CdN$_2$H$_8$ and HgN$_2$H$_8$ were found to be superconductors at ambient pressure and the presence of interstitial electrons suggests that they are also electrides, relative low work functions (3.03, 2.78 and 3.05 eV) implying that they can be used as catalysts for nitrogen reduction reactions as well.
1. Introduction

Superconducting materials attract the attention of scientists because of their zero resistance and anti-magnetic properties,\(^1\) when the temperature of a superconductor falls below its superconducting transition temperature \((T_c)\), it will enter the superconducting state.\(^2\) Therefore, the superconducting transition temperature is the key to determine whether the material can be used in practice.\(^3\) However, most superconductors do not have high \(T_c\),\(^4\) which limits the wide application of superconducting materials and makes the search for high-temperature superconductors become one of the most critical problems in condensed matter physics. Ashcroft et al.\(^5\) predicted that the monomeric H would transform to the metallic state at high pressure with \(T_c\) reaching room temperature, and metallic hydrogen was experimentally observed at the pressure of 495 GPa.\(^6\) However, the pressure required to prepare metallic hydrogen experimentally is too high. Despite it has high superconducting superconducting transition temperature, it is still unfriendly to experimentalists, so it’s necessary to design high-temperature superconductors that can be easily synthesized.\(^7\) In recent years, more and more theoretical work has shown that "chemical precompression"\(^8\) realized by adding other elements to the hydrogen monomers allows the preparation of metallic hydrogen with much lower pressure.\(^9\) For example, the high-temperature superconductors H\(_3\)S,\(^10\) SiH\(_4\),\(^11\) CaH\(_6\),\(^12\) YH\(_6\),\(^13\) and LaH\(_{10}\).\(^14\) However, the synthesis pressure of these hydrogen-rich compounds still has to be more than 100 GPa, meaning that they can only be synthesized in the micron scale in expensive diamond anvil cell,\(^15\) which is still uneasy for experimental synthesis.

Fortunately, ternary hydrides exhibit stronger "precompression" effects, such as LaBH\(_8\),\(^16\) LaBH\(_9\),\(^17\) and LaBeH\(_8\).\(^18\) These compounds are predicted to be potential superconductors and achieve high-temperature superconducting states at relatively low pressures. This implies that they have the potential to be synthesized as millimeter-scale products by inexpensive large volume cubic pressure cells,\(^19\) greatly enhancing the potential for industrial applications. Recently Xiang et al.\(^20\) predicted that KB\(_3\)H\(_8\) obtained by introducing [BH\(_4\)] units into the fcc lattice of potassium could have a \(T_c\) of 146 K at 12 GPa. In addition, Zhong et al.\(^21\) inserted methane into the fcc lattice of Na, K, Mg, Al, and Ga, and theoretically predicted a series of excellent BCS superconductors, such as MgC\(_2\)H\(_8\) (\(T_c = 55\) K, 40 GPa) and AlC\(_2\)H\(_8\) (\(T_c = 67\) K, 80 GPa), which provided us with a reference for designing high-temperature superconductors under mild conditions. Compared to B and C, element N has
similar electronegativity and atomic structure. The difference is the 2p orbital of the N atom can only accept 3 electrons, which means the H atom in [NH₄] cannot form a complete H⁺ ion and has a certain degree to turn into atomic H, which is favorable to turn into a high-temperature superconductor as atomic metallic hydrogen. Therefore, in this work, ammonium ions are attempted to be intercalated inside the fcc lattice to realize chemical precompression of H with the help of N and the other element, making it possible to metallize H at lower pressures, our study providing theoretical guidance for the experimental synthesis of high-temperature superconductors under mild conditions.

2. Computational details
The Vienna Ab-initio Simulation Package (VASP) is used to perform density functional calculations, and the projected-augmented wave pseudopotentials method is employed to describe the electron-ion interaction. Generalized gradient approximation and Perdew-burke-ernzerhof as exchange-correlated functional with a cutoff energy of 900 eV and k-point grid density of 0.03 × 2π based on the Monkhorst-Pack method. The relaxed ionic positions and cell parameters provided energy and forces smaller than 10⁻⁵ eV and 0.002 eV/Å, respectively. The QUANTUM ESPRESSO package (QE) is used to calculate the electron-phonon coupling (EPC) properties in linear response theory, the ultra-soft pseudopotential with a kinetic cutoff energy of 160 Ry and a charge density cutoff energy of 1500 Ry, respectively. Self-consistent field (scf) calculations are performed on a fine k-point grid with a density of 40 × 40 × 40, the Methfessel-Paxton first-order spread is set to 0.01 Ry, and an irreducible q-point grid with a phonon density of 10 × 10 × 10 is used to further calculate the phonon property. The coulomb pseudopotential parameter μ* = 0.10 is used in the modified McMillan-Allen-Dynes equation to estimate the superconducting transition temperature.

3. Results and discussion
The kinetic stability determined by phonon vibrations is a necessary prerequisite for the superconductivity of the compound. Typical pressure points of 10, 30 and 50 GPa were used to test the kinetic stability of the compound XN₂H₈. High-throughput calculations reveal that the fcc lattices of 12 elements are able to remain stable after being intercalated by NH₄. They are Be, Mg, B, Al, Ga, IN, Tl, Zn, Cd, Hg, Cu, and Ag. It is noteworthy that these elements have similar electronegativity (from 1.2 to 1.9) and valence electron numbers (1 or 2). Having a slightly lower
electron negativity than H(2.1) allows the charges on their atoms to migrate to the H atoms, avoiding the electrons being bound to the localized regions of the atoms, leading to the reduced stability caused by the Jahn-Teller effect. Because the Pauling electronegativity of Au is 2.4, this explains the instability of Au in I B group together with Cu and Ag. In contrast, Ca, Sr and Ba, which are in II A group with Be and Mg, are more likely to provide electrons to H due to their smaller electronegativity, leading to the instability caused by localization of electrons on the H atom. The crystal structure of 12 XN₂H₈ can be seen from Table S1 in the supporting materials.

Figure 1. (a) Crystal structure of XN₂H₈. (b) Kinetic stability at 10, 30 and 50 GPa. Pressure-induced electron-phonon coupling parameters λ (c), log-averaged phonon frequency ωlog (d), and superconducting transition temperature Tc (e).

These 12 XN₂H₈ compounds were further detailed to calculate their electron-phonon coupling properties from 0 to 50 GPa. Figures 1(c)-(e) demonstrate the variation of λ, ωlog and Tc with pressure, and surprisingly, three ternary hydrides exhibit high temperature superconductivity (Tc>77K), which are AlN₂H₈ (40 GPa, λ=2.35, ωlog=743.95 K, Tc=118.40 K), MgN₂H₈ (30 GPa, λ=1.86, ωlog=738.87 K, Tc=105.09 K), and GaN₂H₈ (50 GPa, λ=1.43, ωlog=1154.92 K, Tc=104.39 K). For X=Ag (λ=2.87, ωlog=311.33 K, Tc=54.92 K) and Cu (40GPa, λ=2.49, ωlog=466.69 K, Tc=76.65 K), although they have higher λ (Figure 1(c)), the low ωlog (Figure 1(d)) causes the Tc to not reach above 77 K. The strong electron-phonon coupling and the high average phonon frequency may be the reasons for the high Tc.

Pressure not only brings changes to the physical properties but also affects the structure of the crystal. Usually, the pressure makes the lattice more compact and thus leads to a decrease in the
atomic spacing. On the contrary, with increasing pressure, the N-H bond length in [NH₄] increases in this system, which is probably due to the influence of H by the neighboring X atoms.

![Figure 2. Effect of pressure on N-H distance (a), X-H distance (b) in the lattice. Pressure-induced changes in the total Bader charge of X (c), N (d), and H (e) atoms. (f) Scatter plot of Tc vs. average Bader charge per H atoms based on 48 data points.](image)

Figure 2(b) reveals the distances between X and H atoms at high pressure. The increase in pressure makes their distances shorter, and the electron cloud with a higher degree of overlap makes their interactions stronger, the attractive force originating from the X atoms is the possible reason for the shorter N-H bond length. Bader charge analysis was performed to obtain the charge transfer affected by the bond length change. Figures 2(c), (d) and (e) show the total Bader charge for each type of atoms in XN₂H₈. Bader charge of N varies very little, so the pressure does not make the charge on N migrate significantly. Compared to the N atom, the greater pressure causes a significant decrease in the number of electrons on X and a significant increase in the number of electrons on H. This indicates that the pressure causes charge transfer between the X and H atoms, which explains the shortening of the X-H distance. Furthermore, our results reveal the trend of atomization of H in the XN₂H₈ system, where the high electronegativity of N makes it attract the 1s electrons of H to fill the N-2p orbitals in the [NH₄] unit. However, the X atom tends to provide electrons for H due to its lower electronegativity, which makes the [NH₄] unit gain more electrons and become unstable, making it easier for the N-H bond to dissociate and the H⁺ ion to become atomic H, reaching a similar environment as the H atom in metallic hydrogen. The atomization of H⁺ gives electrons at lower levels the opportunity to reach the Fermi level, which may enhance superconductivity. This
conclusion is further verified in Figure 2(f), where the average Bader charges per H (\(\bar{\delta}\)) are -0.218, -0.214, and -0.233e in three high-temperature superconductors AlN\(_2\)H\(_8\), MgN\(_2\)H\(_8\), and GaN\(_2\)H\(_8\), respectively, which are closer to 0 compared to the low \(T_c\) ones. \(T_c\) has a linear scalar relationship with \(\bar{\delta}(H)\). The stronger the tendency of H\(^+\) ions to transform into atomic H, the higher \(T_c\) of this superconductor.

Figure 3. (a), (b) is band structure, density of states, phonon dispersion curves, phonon density of states (PHDOS), and Eliashberg spectral function of AlN\(_2\)H\(_8\) at 40 GPa. (c), (d) is MgN\(_2\)H\(_8\) at 30 GPa. (e), (f) is GaN\(_2\)H\(_8\) at 50 GPa. where the colors in the phonon dispersion curves are weights on \(\lambda\).

Considering the charge transfer between X and H, properties of X may also affect the superconductivity. Figure S1 shows that the highest \(T_c\) of XN\(_2\)H\(_8\)-type compounds is strongly correlated with the first ionization energy of X atoms, this is because the lower the first ionization energy, the easier it is for the electrons on X to break away from the nucleus, and the easier it is for charge transfer to happen between X and H. In addition to charge transfer, outstanding physical
properties will be determined by its electronic structure. Therefore it is necessary to study the electronic structure of superconductors with high $T_c$ to gain physical insight. Despite having different types of X atom and external pressures, their band structures show similar characteristics (Figure 3(a), (c) and (e)), which provide theoretical mechanisms for the design of high $T_c$ superconducting materials. The electronic states of N and H at higher levels are much less than those at lower levels ($< -7$ eV), and N and H located at lower levels have the same trend of DOS, which confirms the existence of N-H bonds in the system. The DOS of X, N and H atoms above 7 eV has a similar trend, indicating a strong coupling between these three types atoms, which is consistent with the characteristics of high-temperature superconductors.\(^{31}\) In addition, the DOS of the X atom appears at the $>-7$eV level instead of the $<-7$eV one because there is some charge transfer and interaction between X and H, but no stable chemical bond is formed. Although the differences in pressure and elements lead to inconsistencies in Fermi surfaces. However, the Fermi surface near the central $\Gamma$-point has a similar spherical shape, which has the same behavior as the Fermi surfaces of AlC$_2$H$_8$ and MgC$_2$H$_8$.\(^{21}\)

The phonon dispersion curves (Figure 3(b), (d) and (f)) reveal the distribution of phonons at different frequencies. From the PHDOS, it can be seen that the low frequency phonons below 15 THz mainly originate from X and N atoms, where the phonons of X atoms are lower than those of N due to the relatively larger atomic masses of Al, Mg, and Ga. The lower atomic mass of the H atom allows it to dominate the PHDOS for high-frequency phonons above 15 THz, the contributions of high-frequency phonons above 15 THz to $\lambda$ are 51%, 60%, and 71%, respectively, indicating that the H atom dominates the electron-phonon coupling. Similarly, the phonons around 30 THz at the $\Gamma$ point contribute significantly to the EPC. In addition to this, phonon softening is observed near the X point on AlN$_2$H$_8$.\(^{21}\)
Figure 4. (a) Visualization of the electron localization function (isosurface=0.6). (b)-(d) Electron localization function for 2D plane (hkl=1,0,-1). (e)-(g) Work functions of ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$ on the surface of (001), noting that (100), (010) and (001) are equivalent. Our results also reveal that ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$ can remain stable and superconducting at ambient pressure ($T_c$=0.33, 0.20, and 0.01 K), which expands the range of ambient superconducting materials. It is noteworthy that the lattices composed of Ga, In, and Tl, which are very similar to the atomic structures and electronegativity of Zn, Cd, and Hg, are unstable at ambient condition, implying that there may be exotic charge distributions in ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$. The electron localization function (ELF)\textsuperscript{32} provides an explanation for their stability with the formation of localized interstitial electrons between [NH$_4$] units (Figure 4(a)). According to the suggestion of Hosono et al.\textsuperscript{33} the ELF of ternary compounds can take the value of 0.49-0.79, so the ELF in this work is 0.6, the presence of interstitial electrons implies that they belong to electrides. Figures 4 (b)-(d) reveal the origin of the interstitial electrons. Since the 2p orbital of N can only hold up to 3 electrons, it cannot fully accept the 1s electrons from the surrounding 4 H atoms, and the surplus electrons on [NH$_4$] enter the interstitial to reduce the total energy of the system, making the lattice more stable and acting as an interstitial quasi-atom (ISQ).\textsuperscript{34} Figure S2 shows that GaN$_2$H$_8$, InN$_2$H$_8$, and TIN$_2$H$_8$ do not show interstitial electrons at 0 GPa and therefore they cannot be stabilized at 0 GPa.
In addition, electrides can be used as catalysts,\textsuperscript{35} and the activity of catalysts is related to the work function,\textsuperscript{36} so the work functions ($\Phi_{WF}$) of ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$ on the Z-direction (001) surface were also calculated (Figure 4(e)-(g)). Their work functions are 3.03, 2.78 and 3.05 eV, respectively, which are much lower than those of Al (4.28 eV) and Y$_5$Si$_3$ (3.5 eV)\textsuperscript{37} and very close to the $\Phi_{WF}$ of lithium metal (2.9 eV). In the catalytic process of nitrogen reduction reaction (NRR),\textsuperscript{38} N$_2$ gains an electron for dissociation is decisive step, and the lower work function means that N$_2$ can gain electrons more easily, our results suggest that the electronic compounds ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$ can be used as potential NRR catalysts.

4. Conclusion

In this work, the metallization of hydrogen was achieved by inserting ammonium ions into the fcc lattice under low pressure conditions, and high throughput calculations revealed that the fcc lattice of 12 elements can have superconducting states in the range of 0-50 GPa. The superconducting transition temperatures of AlN$_2$H$_8$, MgN$_2$H$_8$, and GaN$_2$H$_8$ can reach up to 118.40, 105.09 and 104.39 K, respectively. Bader charge and bond length analysis reveals the physical origin of high-temperature superconductivity, and the high $T_c$ is most likely brought about by the atomization of H. The high $T_c$ is most likely caused by the atomization of H. In addition, our results identify three superconductors at 0 GPa: ZnN$_2$H$_8$, CdN$_2$H$_8$, and HgN$_2$H$_8$, where the interstitial electrons make them also electrides and the presence of a relatively low work function means that they can be used as potential NRR catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary materials to this article can be found online.

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