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PAPER

Possible high- $T_{\rm C}$ superconductivity at 50 GPa in sodium hydride with clathrate structure

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Abstract

Ambient-pressure room-temperature superconductivity is one ultimate goal of science, for it will bring worldwide revolutionary changes in all kinds of technology. Several room temperature and near room temperature hydride superconductors at ultra high pressure (≥ 100 GPa) have been predicted theoretically. In particular, the hydrogen sulfide (H₃S) with $T_C \simeq 203$ K at 200 GPa has soon been confirmed experimentally, establishing a milestone toward room temperature superconductivity. However, high- T_C superconductors at lower pressure (≤ 100 GPa) have not been reported before. In this work, we present high- T_C superconductivity of 180 K at a relatively low pressure of 50 GPa in sodium hydride clathrate structure NaH₆. The T_C can be raised up to 206 K at 100 GPa, similar to the T_C of H₃S but at a much lower pressure. At 200 GPa, it reaches the highest T_C of 210 K, slightly higher than that of H₃S. The strong electron–phonon coupling strength given by the T_{2g} phonon mode at Γ point plays the key role in superconductivity. Our work demonstrates theoretically that hydrides could stabilize at a relatively low pressure and host high- T_C superconductivity.

Ambient-pressure room-temperature superconductivity is one of the ultimate goals of science. It is not only extremely useful in applications that can bring worldwide revolutionary changes in all kinds of technology, but also represents a fertile ground for comparing various high- $T_{\rm C}$ models [1–7]. Unconventional superconductors such as cuprates and iron-based superconductors have drawn tremendous research efforts [8–15]. The origin of high- $T_{\rm C}$ is usually attributed to strong correlations among electrons or strong spin fluctuations [16–19], however the true mechanism remains elusive. On the other hand, conventional superconductors such as MgB₂ with $T_{\rm C}$ originated from electron–phonon coupling based on Bardeen–Cooper–Schrieffer (BCS) theory also attract intensive studies [20–25]. Recently a milestone record of $T_{\rm C} = 203$ K in hydrogen sulfide [26–28] and $T_{\rm C} = 260$ K in lanthanum hydride [29–33] mediated by strong electron–phonon coupling is achieved around 200 GPa, boosting further attention on hydrogen-based superconductors at high pressure.

There is a long history on pursuing room temperature superconductivity in the lightest element, hydrogen. The metallic phase of hydrogen was predicted by Wigner and Huntington in 1935 [34]. Thirty years later in 1968, Ashcroft suggested that solid metallic hydrogen might be a room temperature superconductor [35]. Recent *ab initio* calculations demonstrate similar room temperature superconductivity in metallic hydrogen at extremely high pressure (500 GPa) [36, 37]. The basic idea of high- $T_{\rm C}$ in solid hydrogen is that hydrogen ions with the lightest atomic mass can strongly increase the Debye temperature



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and phonon frequency. Moreover, the high density of state at the Fermi level under high pressure can induce strong electron–phonon coupling [35]. These two conditions play crucial roles in BCS theory toward room temperature superconductivity.

Unfortunately the ultra high pressure required for metallic hydrogen is very difficult to achieve in experiments. A report claims the metallic hydrogen has been synthesized, however more details need further confirmations [38]. Therefore, many hydrogen-based compounds with high- $T_{\rm C}$ have been proposed because the additional ions can play the role to stabilize the lattice structure at relatively lower pressure. H₂S is firstly proposed to be metalized and stabilized under 160 GPa [28]. Then H₃S [26–28] and LaH₁₀ (including the rare-earth series REH₆, REH₉, REH₁₀) [29–33, 39] are predicted to be electron–phonon superconductors. Soon after the theoretical predictions, high- $T_{\rm C}$ superconductivity of H₃S and LaH₁₀ are realized by experiments, demonstrating the powerful ability to predict conventional superconductors by BCS–Eliashberg theory. In addition, more accurate calculations such as solving the Eliashberg equation [40], including the anharmonic correction [41], and so on (see the method section S-I in supplementary information (https://stacks.iop.org/NJP/23/093007/mmedia)) have also been reported. On the other hand, superconductivity of $T_{\rm C}$ up to 100 K [42–44] are discovered experimentally in H₃P under 100–250 GPa first, and soon followed by theoretical calculations of $T_{\rm C} = 70-80$ K [45–47] compatible with previous experimental data.

The hydrogen clathrate structure (HCS) was firstly proposed for CaH₆ [48]. Soon HCS hydrides form a special category with high- T_C including YH₆ [39, 49], YH₉ [39], YH₁₀ [29, 39], LaH₁₀ [29, 39], MgH₆ [50], CaH₆ [48], and LiMgH₁₆ [51]. These HCS are composed of uniform convex tessellation with metallic ions being the electron donor and lattice frame basis. Meanwhile, most of recent high- T_C hydrides are in cubic structure with high crystal symmetry, matching Matthias's empirical rules for seeking BCS superconductors [52]. However, significant difficulties in experiments and real applications remain owing to the required high pressure from 100 to 450 GPa.

In this letter, we demonstrate theoretically that sodium hydride NaH₆ in the truncated cubic cellulation structure exhibits high- $T_{\rm C}$ of 180 K at relatively low pressure of 50 GPa with respect to the extremely high pressure of hundreds of GPa required for the aforementioned high- $T_{\rm C}$ hydrides. Moreover, the $T_{\rm C}$ of NaH₆ can be further enhanced to 206 K by raising the pressure to 100 GPa, which is similar to $T_{\rm C} = 203$ K of H₃S at a much higher pressure of 200 GPa. At 200 GPa, NaH₆ reaches the maximum $T_{\rm C}$ of 210 K, slightly higher than that of H₃S. The relatively low pressure of 50 GPa is experimentally much more achievable than H₃S at 200 GPa [27], thus serves as an important step toward ambient-pressure room-temperature superconductivity.

Sodium, the amplest element of group I alkali metals, is the sixth most abundant species in Earth's crust and widely exists in numerous minerals such as rock salt. Because of the low electronegativity, the single valent *s*-electron can readily donate to the HCS. To search for high- T_C superconductors with high-abundance highly-donating metal ions in the HCS, we study the electronic structure and phonon spectrum of NaH₆ through first-principles calculations based on density functional theory (DFT) and density functional perturbation theory (DFPT) (supplementary information S-I presents the computational details and introduces some advanced electron–phonon-coupling methods [21, 41, 43, 53–57]). The crystal structure of sodium hydride NaH₆ in the cubic HCS with high crystal symmetry (*Pm-3m*) is shown in figures 1(a) and (b). This structure, which is the same as that of the topological Kondo insulator SmB₆ [58–64], has been reported in a previous work [65]. However, the dynamical stability, electron–phonon coupling, and superconductivity have not been studied through DFPT yet [66, 67]. On the other hand, a previous study based on neural network research [68] has shed light on possible T_C higher than 100 K for the Na–H system, being compatible with our *ab initio* study.

Under 50 GPa, the optimized lattice constant of NaH₆ is a = 2.98 Å with the long (short) hydrogen bond length of 1.50 Å (0.85 Å) longer than 0.74 Å of H₂ gas molecules. Owing to sodium's low electronegativity, the HCS receives additional electrons from Na to stabilize the stretched H–H bonds. Even though the extra electrons occupying the hydrogen anti-sigma (σ^*) bond stabilize the stretched H–H bonds, they are actually weaker than the shorter H–H bonds in the molecular phase. Consequently these weaker H–H bonds in the HCS are easier to vibrate and hence can enhance the electron–phonon coupling strength [39] in NaH₆. With the pressure increased to 100 GPa (200 GPa), the lattice parameter decreases to a = 2.78 Å (2.56 Å); meanwhile, the short and long H–H bonds become 0.84 Å (0.81 Å) and 1.37 Å (1.24 Å), respectively.

The electronic band structures and density of states (DOS) of NaH₆ are shown in figures 1(c) and (d), respectively. There is a three-fold degenerate electron band around 2.16 eV above the Fermi level at Γ -point. This degeneracy gives rise to spikes in DOS. Driven by the T_{2g} phonon mode, these spikes march toward the

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Fermi level and offer strong electron-phonon coupling owing to the severely changing electronic properties when this electron pocket passes through the Fermi level.

To date, all the available high- $T_{\rm C}$ hydrides require high pressure from 100 GPa to 450 GPa. In strong contrast, the phonon spectra of NaH₆ at 50 GPa as shown in figures 2(a)–(c) are well-behaved without imaginary (negative) mode, demonstrating that NaH₆ keeps stable at this relatively low pressure. Furthermore, the $T_{\rm C}$ remains surprisingly high of 180 K. Such a high- $T_{\rm C}$ at relatively low pressure, which is an important breakthrough toward ambient-pressure room-temperature superconductor, has never been reported before.

As the pressure raises, the overall band width of the phonon spectra increases from 90 to 115 THz as shown in figures 2(a)-(f), which helps enhance $T_{\rm C}$. Under 200 GPa, the Eliashberg function $\alpha^2 F(\omega)$ exhibits a large optical band at low frequency region with the peak value around 40 THz (\approx 1900 K). The integrated electron–phonon coupling strength $\lambda(\omega)$ increases strongly in this region. The average phonon frequency $\omega_{\rm ln} \sim 1700$ K is nearly equal to $\omega_{\rm ln} \sim 2000$ K of the metallic hydrogen [36]. This is one important reason that NaH₆ yields high- $T_{\rm C}$. The strongest electron–phonon couplings originate from a special T_{2g} mode at Γ with frequency of 33 THz. These strong electron–phonon couplings concentrated in few phonon modes at Γ are the same as those in other HCS such as YH₁₀ [39]. The atom-decomposed phonon bands illustrate that vibrations among H ions, i.e. over the HCS, is the main cause of the strong electron–phonon coupling. While Na ions contribute negligibly on the low frequency phonons, serving as electron donors and cornerstones of HCS only. Because of the additional constraint that the size of the embedded cation should well match the cage-like HCS, replacing Na by Li, K, Mg, and Ca all results in unstable structures with negative phonon bands.

Figures 2(g)-(i) show the real space movement pattern of the three-fold degenerate T_{2g} phonon modes with the strongest electron-phonon coupling around 33 THz at Γ . The vibrations of the hydrogen octahedron indicated by the red arrows show that each hydrogen pairs located at opposite corners vibrate antiparallel along the same direction. Similar to the conclusion given by phonon band structures, the partial charge around the Fermi level (-0.3-0.3 eV) over the HCS (figure 2(j)) gives a consistent picture of the crucial role in superconductivity that HCS takes part. Furthermore, in comparison with figures 1(a) and (b), these electrons actually locate over the long H–H bonds only, indicating that the long hydrogen bonds, rather than the short ones, are the main cause of the high- T_C in NaH₆. The electron–phonon coupling



induced changes in electronic structures through frozen-phonon simulations are illustrated in supplementary information S-II.

Figure 3 compares the electron–phonon coupling strength λ (see supplementary information S-III for convergence test), logarithm average phonon frequency ω_{ln} , superconducting T_C , and DOS at the Fermi level of NaH₆ and H₃S [26, 27]. The superconducting T_C of NaH₆ (figure 3(a)) increases significantly from 180 K at 50 GPa up to 206 K at 100 GPa, and then increases gently up to 210 K at 200 GPa. Except at 50 GPa, all the obtained T_C above 100 GPa are slightly higher than that of H₃S. Nevertheless, the



Figure 3. (a) The DOS at the Fermi level (blue) and the superconducting $T_{\rm C}$ (red) of NaH₆ as functions of pressure. The red horizontal dashed line indicates the $T_{\rm C} = 200$ K of H₃S at 200 GPa [26, 27]. (b) The electron–phonon coupling λ (blue) and the logarithm average phonon frequency $\omega_{\rm ln}$ (red) of NaH₆ as functions of pressure. The blue (red) horizontal dashed line denotes the electron–phonon coupling (logarithm average phonon frequency) of H₃S at 200 GPa [26, 27]. The grey color (below 50 GPa) indicates the unstable NaH₆ lattice region.

 $T_{\rm C} = 180$ K of NaH₆ at 50 GPa remains surprisingly high. This high- $T_{\rm C}$ at low pressure is important toward room-temperature superconductivity at ambient-pressure. Meanwhile DOS at the Fermi level decreases monotonically with increasing pressure, indicating that the DOS factor is actually harmful to $T_{\rm C}$. On the other hand, λ and $\omega_{\rm ln}$ (figure 3(b)) are respectively suppressed and strengthened by raising the applied pressure. These opposite trends in λ and $\omega_{\rm ln}$ is the reason why $T_{\rm C}$ increases only slightly above 100 GPa. Furthermore, in comparison with H₃S at 200 GPa, $\omega_{\rm ln}$ (λ) of NaH₆ is larger (smaller) than that of H₃S. These different behaviors are given by different lattice and electric natures between NaH₆ and H₃S. The H₃S lattice is composed of interpenetrating cubes with H–S bonds, whereas the NaH₆ crystal is of the HCS nature with weak H–H bonds enhancing the hydrogen vibration $\omega_{\rm ln}$.

The NaH₆ hydride exhibits several properties similar to those of other high- $T_{\rm C}$ hydrides, including the high symmetry crystal, cubic lattice, HCS, and metallic ions. To compare with previous cases, we present the $T_{\rm C}$ -pressure phase diagram of available high- $T_{\rm C}$ hydrides in figure 4(a). It can be clearly seen that NaH₆ is the only superconductor presenting high- $T_{\rm C}$ over 200 K at pressure below 100 GPa. Another Na hydride NaH₈ studied in this work also exhibit high- $T_{\rm C}$ of 130 K at 100 GPa (supplementary information S-IV). Except the metal hydrogen with 350 K over 500 GPa, all the other superconductors with $T_{\rm C} > 200$ K are in the cubic structure. Moreover, for hydrides with $T_{\rm C} > 200$ K (green region), except H₃S [26], all the others (CaH₆ [48], MgH₆ [50], YH₆ [39, 49], YH₉ [39], YH₁₀ [29, 39], LaH₁₀ [29, 39], ThH₁₀ [78], AcH₁₀ [78], AcH₁₆ [79]) are in the HCS and the degenerate phonon modes at Γ plays the crucial role in high- $T_{\rm C}$ superconductivity. This kind of enhanced superconductivity has been observed in other types of clathrate-like structures such as the potassium-doped carbon Fullerenes K₃C₆₀ [84] and β -pyrochlore K_xOs₂O₆ oxide [85]. The above trends imply that simple cube, BCC, and FCC sublattice of metal ions situated at the center of cubic-cellulation hydrogen cages may pave a possible route toward ambient-pressure room-temperature superconductivity.

Figure 4(b) shows the pressure-hydrogen bond lengths diagram for available high- $T_{\rm C}$ hydrides in HCS. Interestingly, all the H–H bonds, even though in different kinds of hydrides, show the similar trend that



Figure 4. (a) Superconductor phase diagram of available high- $T_{\rm C}$ hydrides. The red solid (empty) spheres are for NaH₆ (NaH₈) from our calculations. The blue circles are given from previous studies [26, 27, 29, 35–37, 39, 42, 46, 48–50, 53, 69–80]. The yellow crosses are experimental results [27, 30–33, 81–83]. The light-grey region indicates pressure below 100 GPa. The green region denotes hydrides in HCS with $T_{\rm C}$ higher than 200 K. The blue region is for other hydrides without HCS with $T_{\rm C}$ below 200 K. (b) The pressure-hydrogen bond lengths diagram for HCS. The blue circle indicates the H–H bond length of available hydrides. The red solid circle (square) indicates the NaH₆ long (short) H–H bond length at different pressure. The long H–H bonds, rather than the short ones, take part in the $T_{\rm C}$ mechanism. The bond lengths of NaH₈ are also presented in red empty circle. (c) The relation between the bond length and $T_{\rm C}$.

they approximately lie on a straight line, demonstrating the close relation between the pressure and H–H bond lengths. The long H–H bonds of NaH₆, which dominate the high- $T_{\rm C}$ mechanism as discussed previously, do follow this simple rule with relatively long bond length at low pressure. The only exception is the short H–H bonds in NaH₆ that they locate far away from all the others because they do not take part in the high- $T_{\rm C}$ mechanism of NaH₆. Combining the bond length–pressure relation in figure 4(b) with the bond length- $T_{\rm C}$ relation in figure 4(c), the implication for designing high- $T_{\rm C}$ hydrides at lower pressure is clear: to search for a HCS with suitable metal ions matching the size of the H-cage yielding longer H–H bonds. Here we note that both the short and long H–H bonds with suppressed covalent charge over the H–H long bonds and eventually break the covalent behavior over the H–H long bonds, resulting in lattice instability below 50 GPa. On the other hand, one should look for shorter H–H bonds if higher $T_{\rm C}$ is the only concern without the lower-pressure constraint. There is usually a competition between stability, electron–phonon coupling strength, and crystalline symmetry in hydrides under pressure. It could be fortuitous that NaH₆ remains stable at relatively low pressure of 50 GPa while with strong electron–phonon

coupling and crystalline symmetry. Future studies may resolve if such good behavior can also be discovered in other hydrides.

Inspired by the McMillan formula (equation (2), S1) that both the electron–electron interaction μ^* and electron–phonon coupling strength λ play important roles in enhancing $T_{\rm C}$ through the exponential function, we assume that the complicated argument in the exponential function may have simple correlation with the H–H bond length *L*. We thus fit the available hydrogen bond length- $T_{\rm C}$ data of high- $T_{\rm C}$ hydrides in HCS shown in figure 4(c) by the simple relation: $T_{\rm C} = A \exp(-B \cdot L)$. Surprisingly, the fitting is good as depicted in the grey dashed curve in figure 4(c) with A = 1160 K and B = 1.37 Å⁻¹. All the relevant data points locate closely to the fitted curve. Here by relevant we mean the H–H bonds formed by electrons around the Fermi level that contribute significantly to high- $T_{\rm C}$. The irrelevant short H–H bonds of NaH₆ (solid red square) and long H–H bonds of YH₉ [39] (not shown here) indeed lie away from this curve. As such, this simple relation between H–H bond length and $T_{\rm C}$ can give a quick hint on $T_{\rm C}$ of hydrides in HCS.

In conclusion, by using DFT and DFPT calculations, we theoretically demonstrate that NaH₆ in HCS exhibits the highest T_C of 210 K at 200 GPa. It remains stable at a relatively low pressure of 50 GPa while hosts a surprisingly high T_C of 180 K. In comparison with the extremely high pressure required for other hydrides, such a high- T_C at low pressure is a significant achievement toward normal conditions. The strong electron–phonon coupling is dominated by the three-fold degenerate T_{2g} phonon at Γ , which also play the key role of enhancing T_C in previous studies. More importantly, our study shed light on guidelines for designing high- T_C hydrogen-based superconductors at low pressure: to search for a HCS with suitable metal ions matching the size of the H-cage yielding longer H–H bonds, which paves a possible route toward ambient-pressure room-temperature superconductivity.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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