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Emergence of Near Room-temperature Superconductivity in Hydrides with H₂ molecular units

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ABSTRACT

The achievement of high-temperature superconductivity in compressed hydrides with extended lattices, e.g. H₃S and LaH₁₀, has become a milestone in the quest for room-temperature superconductivity. For realizing room-temperature superconductivity lattices where hydrogen adopts multi-centered bonds are deemed as indispensable, while hydrides containing H₂-molecular units are believed to be unfavorable. Here, we report newly discovered H₂-molecular-type hydrides with an exceptional near room-temperature superconductivity of 270 K in compressed NaH₁₀ and a T_c of 152 K in NaH₁₂, where H atoms solely constitute H₂ units, and Na-H form ionic bonds. Our first-principles calculations unveil that the high- T_c is mainly attributed to strong electron-phonon coupling stemming from the large electron-phonon matrix element driven by medium-frequency interatomic interactions and high-frequency H-derived phonon softening caused by Fermi surface nesting, thus scattering itinerant electrons to form Cooper pairs. Of particular note, we reveal that the unique delocalized background charges cooperate with others electrons occupying the pressure-induced *sp*-hybridized antibonding bands of molecular H₂-units act as itinerant electrons to mediate metallic interactions and participate in electron-phonon coupling. This discovery reshapes the understanding of superconductivity dominated by molecular H₂-units, provides new insights for elucidating phonon-mediated superconductivity and raises broad prospects of realizing room-temperature superconductivity in molecular hydrogen-based superconductors.

The quest for new superconducting materials and the elucidation of their microscopic mechanism of superconductivity has been a grand challenge [1,2] ever since Kamerlingh Onnes' first ground breaking experiments. Ashcroft proposed that the lightest element, hydrogen, would evolve into a metallic solid phase at high pressures, and its high phonon frequencies and robust electron-phonon coupling (EPC) would be a key ingredient required to achieve high- T_c phonon-mediated superconductivity [3]. Despite great experimental strides, it's still debated if a high-pressure phase of solid metallic hydrogen has been made in diamond anvil cells, and the huge pressures required to metalize hydrogen in the solid have challenged the capability of current experiments [4,5]. Hydrides, subsequently, were selected as alternative candidate materials for exploring high- T_c superconductivity ever since Ashcroft proposed that chemical precompression [3,6] can lower the pressure required for metallization. Extensive theoretical studies have predicted a number of binary hydrides with high critical superconducting temperatures (T_c s), finding two general classes of superconducting materials [7-12]. The first includes *p*-block elements that bond with hydrogen covalently in novel proportions, for example H_3S , which was the first hydride found experimentally and theoretically nearly simultaneously to attain a record-breaking T_c of 203 K at 155 GPa [7,13]. The second includes electropositive metal elements whose valence electrons are transferred to hydrogenic lattices. In particular, experiments have verified predictions of high- T_c superconductivity in phases with clathrate-like lattices such as YH_9 (243 K at 200 GPa), LaH_{10} (260 K at 180 GPa) [14-19], and CaH_6 (215 K at 172 GPa) [20,21]. These 3-dimensional clathrate-like hydrogen lattices, with multi-centered hydrogen bonds, are deemed as being indispensable to exceptional superconductivity [2].

However, with the exception of molecular hydrogen, hydrides that contain H_2 -units are not known to possess the highest T_c under pressure. The predicted T_c of molecular H-III phase (*Cmca*-12) is 242 K at 450 GPa [22]. The H_2 -unit-constituted *Ama*2- GeH_4 and *P6₃/mmc*- SnH_4 phases are predicted to possess T_c 's of 57 K and 62 K, and H_2 -units are considered to play a dominant role in improving the EPC [23,24]. In addition, $SiH_4(H_2)_2$ and $GeH_4(H_2)_2$ containing more H_2 -molecule units are synthesized with theoretically predicted T_c 's of 107 K and 90 K [25,26]. Nevertheless, the near room-temperature superconductivity is never obtained in H_2 -molecular hydrides, and instead, hydrides containing H_2 -units have recently been regarded as an unfavorable factor for superconductivity [2,27]. Whether the H_2 -molecular structure can induce a robust EPC and (near) room-temperature superconductivity in hydrides has not yet been determined and remains challenging.

The metallization of phases containing H_2 -units can be understood via considering the knowledge of compressed alkali metal polyhydrides [28]. Being attributed to the transfer of valence electrons from the electropositive metal to $H_2-\sigma^*$ -orbitals thus partial filling the $H_2-\sigma^*$ -bands, the *R-3m*- LiH_6 phase generated a high density of states (DOS) at the Fermi level (ϵ_F). Meanwhile, "Madelung precompression" generated a smaller volume than what would be expected at relatively low pressures [28]. The pressure-induced broadening and overlap of H^- and $H_2-\sigma^*$ -bands metallize the *Pm*- NaH_9 phase [29,30]. In KH_5 and RbH_5 species with H_3^-

counter anions and H₂ bystander molecules, metallization occurred via pressure-induced widening and the final overlapping of the filled H₃⁻ non-bonded band with the metal *d*-bands [6,31,32]. The potential T_c of phonon-mediated H₂-molecular-type hydrides is markedly influenced by the DOS at ε_F . Intriguingly, we noticed an additive inconsistency between the total DOS and the sum of discrete DOS for different elements in the electronic structure of SbH₄ [33], which are composed of H₂ units (see Fig. S1). This discrepancy results in the emergence of novel background charges [33,34]. To investigate whether the background charge as a free electron participates in the EPC and induces high-temperature superconductivity holds significant research value in elucidating phonon-mediated superconductivity for H₂-molecular-type hydrides. Herein, we proposed a high-throughput structural search approach to screen H₂-molecular-type hydrides to quickly identify potential high- T_c superconductors based on the presence of background charges near the ε_F [see Fig. 1(a)]. Application of the proposed method identified and confirmed H₂-molecular-type hydrides NaH₁₀, TeH₄ and SnH₁₄ possessing background charges near the ε_F [30,33,35]. We take the compressed NaH₁₀ as representatives to investigate superconductivity, elucidate the influence of background charges on superconducting behavior, and tackle the challenge of achieving room temperature superconductivity in H₂-molecular-type hydrides.

In this Letter, we confirmed a pressure-induced H₂-molecular-type superconductor, NaH₁₀, with a T_c of 270 K at 4 Mbar, possessing an unexpected near room-temperature superconductivity. Our first-principles calculations illustrate that large electron-phonon matrix elements are driven by the diverse medium-frequency interatomic interactions, aided via high-frequency H-derived phonon softening caused by FS nesting that scatters itinerant electrons to form Cooper pairs. Notably, these itinerant electrons partially act as delocalized background charges and partially occupy the pressure-induced *sp*-hybridized antibonding bands of H₂-units to participate in EPC. Further testing the presence of H₂-molecular-type hydrides on the resulting superconductivity, we doped sodium into the H-III phase. Our computational experiment yielded a dynamically stable *R*-3*m*-NaH₁₂ structure with a T_c of 154 K at 150 GPa, where itinerant electrons occupied *sp*-hybridized orbitals showing delocalized characteristics. These results demonstrate that near room-temperature superconductivity is indeed possible in H₂-molecular-type hydrides. Our study reshapes the traditional understanding of superconductivity dominated by H₂-units and provides new insights for elucidating phonon-mediated superconductivity in molecular hydrogen-based superconductors.

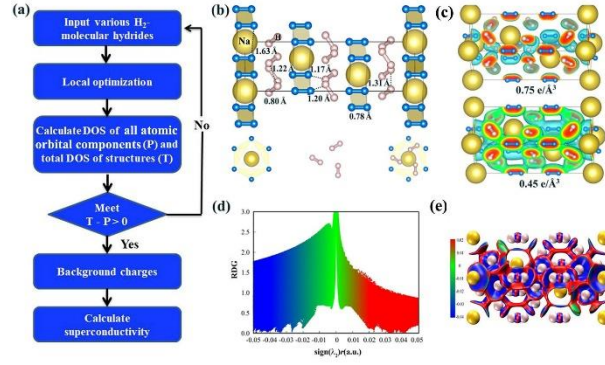


Fig. 1. (a) Schematic illustrating the methodology for identifying potential H₂-molecular-type hydrides with high- T_c . (b) The R32-NaH₁₀ phase at 300 GPa and (c) 3D isosurface of the electron localization function (ELF). (d-e) Plots of the reduced density gradient (RDG) vs electron density (ρ) in terms of the sign of the second Hessian eigenvalue (λ_2) [36].

Our enthalpy calculation identified that molecular hydride NaH₁₀ is stabilized above 200 GPa with dynamical stability and has a relatively higher enthalpy than NaH₉ + 1/2H₂ compounds [37] (see Fig. S2 and Scheme S2 [38]). Notably, NaH₁₀ lives on the convex hull when the pressure is above 360 GPa. At 300 GPa, the H–H bond lengths of 0.78 ~ 0.80 Å indicate typical H₂-molecular characteristics, as shown in Fig. 1(b) [23]. Along the c axis, this structure includes three alternate layers of sodium intercalated hydrogen molecules, three-molecular rings with unbound molecular hydrogen and elongated H₂-molecules. The distance between adjacent H₂-units, > 1.17 Å, is much larger than the bond length of H₂ gas at ambient conditions, 0.75 Å. The Na–H distance falls between 1.67 - 2.72 Å, suggesting that NaH₁₀ is an ionic crystal. In Fig. 1(c), there is no ELF value at the interval of the H₂-units when adopt the isosurface of 0.75 e/Å³, suggesting that there are no covalent interactions. But metallic bonds have been formed in Fig. S3, as evidenced by the distribution of the free electrons at an isovalue of 0.45 e/Å³.

To reveal the precise interactions between H₂-units, we calculated the key index, RDG defined as $1/6\pi^2|\nabla\rho|/\rho^{4/3}$ in Fig. 1(d), where ρ represents the electron density. Abundant spikes have large negative values of $\text{sign}(\lambda_2)\rho$, and RDG trends to zero, characterizing the noncovalent interactions between H₂-units [50]. For the symmetrical distribution of weak chemical bonding, the vdW interactions located in a ρ range of -0.01–0.01 a.u with negative and positive values of $\text{sign}(\lambda_2)$. The apparent spikes of RDG corresponding to $\text{sign}(\lambda_2)\rho$ associated with positive $\text{sign}(\lambda_2)$ value greater than 0.03 a.u. indicate that steric effects, repulsive interactions, exist in inter molecular positions of H₂-units, implying that there are electrons occupying its antibonding molecular orbital. These results are also confirmed in Fig. 1(e), where the colors of dark-blue and red are corresponding to attractively ionic and repulsively electrostatic interactions, respectively.

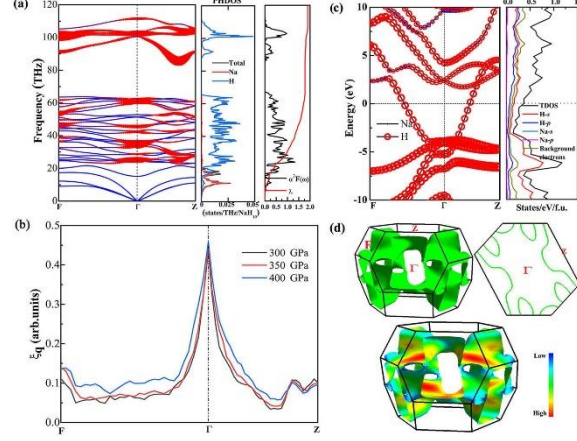


Fig. 2. (a) Phonon dispersion curves, phonon density of states (DOS) and Eliashberg spectral function $\alpha^2F(\omega)$ together with the integral $\lambda(\omega)$ of R32-NaH₁₀ phase at 300 GPa. The size of the solid dot on phonon spectra signifies the contribution to the line width. (b) The calculated nesting function ζ_q with pressure evolution along special q trajectories. (c) Electronic band structure and projected DOS. (d) The FS (upper) and corresponding Fermi velocity (bottom).

To estimate the superconductivity of the R32 phase, we have applied Allen-Dynes modified McMillan equation based on harmonic approximation to calculate the T_c [51]. For pressure at 300 GPa, the phonon dispersion curves, partial phonon DOS, $\alpha^2F(\omega)$ and EPC λ have been displayed in Fig. 2(a). The high-frequency phonons corresponding to the vibration modes of H₂-units are confirmed in Fig. S4, reflecting that this phase is mainly composed of H₂-units. The high-frequency vibrations are consistent with the vibrational frequencies of molecular hydrogen in the H-III phase, especially above 90 THz, which is vastly different from the *I*₄₁/*amd*-H-IV phase of metallic hydrogen containing atomic-H sublattices at 500 GPa [52,53]. Combined with the $\alpha^2F(\omega)$ and the partial phonon DOS analysis, the most significant contributions, ~80% to the EPC, stem from diverse interatomic interactions identified in Fig. S4, accumulated in medium-frequency vibration modes within 25–65 THz. On the other hand, the vibration modes above 90 THz only contribute 6.36% to EPC. Medium-frequency optical phonon vibrations play a major role in scattering electrons forming Cooper pairs and enhance T_c , which can be proved by the peaks of $\alpha^2F(\omega)$, and integral $\lambda(\omega)$ and projection line width γ_{qv} . However, the

contribution from the low-frequency translational vibrations constitutes 13.64% of the integral λ . The corresponding T_c of 238 K estimated with $\mu^* = 0.1$ is close to LaH₁₀ of 254 K. Particularly, the average phonon frequency $\omega_{\log}$ and λ reached 1443 K and 1.86, respectively. Compared with the vibrational characteristics and EPC of LaH₁₀ at 300 GPa, the $\omega_{\log}$ of NaH₁₀ is close to the 1488 K obtained for LaH₁₀, and $\lambda(\omega)$ is higher than the 1.78 calculated for LaH₁₀ [15], pointing out two important factors inducing the R32-NaH₁₀ phase to possess a high- T_c . The ability of R32-NaH₁₀ to possess a high average phonon frequency is mainly attributing to the shortest H–H bond length of only 0.78 ~ 0.80 Å, severely shorter than atomic hydrogen-type *Fm*-3*m*-LaH₁₀, where $r_{\text{H-H}} > 1.0$ Å. The relatively large EPC of NaH₁₀ prompted us to investigate the reasons affecting the intensity of electrons scattered by phonons. Next,

our research mainly focuses on the analysis of the electronic properties and phonon characteristics, traced back to the Hopfield expression, $\lambda = \frac{N(\varepsilon_F)\langle I^2 \rangle}{M\omega^2}$, to further unveil the features of EPC interaction and superconductivity [54].

Regarding the $N(\varepsilon_F)$ term arising from the electronic properties in Fig. 2(c), significantly, we revealed a new mechanism of background charge participating in the EPC observed in the projected DOS, that is, valence electrons being ionized and delocalized caused by high-pressure, forming a distributed environmental charge density to mediate metallic interactions. This result is completely different from the formation mechanism of interstitial quasi-atoms in compressed lithium and sodium, which show insulating properties [55,56]. In fact, the increased kinetic energy of the electrons induced by pressure here exceeds the limit of coulomb potential field, which makes the partial charges redistribute in the lattice as background charges, and this analogous scenario also occurred in the atomic metallic H-IV phase (*I4₁/amd*) with a predicted T_c of 356 K at 500 GPa [52]. The projected DOS illustrates that high-pressures induce the filling of H-*p* orbitals and form *sp*-hybridized states, which cooperate with the background charges to mainly constitute the FS. The hydrogen atoms in NaH₁₀ with *p*-electron occupied orbitals exhibits the characteristics of 2*p*-block elements, implying that multiple band pairings of *s*- and *p*-electronic states cross ε_F relative to *s*-block element H (see Fig. S6) [57]. In Fig. S7, a large EPC also benefited from the high-DOS at ε_F caused by a Van Hove singularity, which is mainly constituted with H-*sp*-hybridized states and background charges where they make the 58% and 42% contribution to the total DOS, respectively [57,58]. These *sp*-hybridized states are expected to have higher freedoms of orbital multiplicity and more easily to form stable Cooper pairs than H-*s*-electrons [59,60]. And Fig. S10 further confirmed that the background charges mainly participate in EPC due to the total $N(\varepsilon_F)$ of background charges increased with the pressurization.

Regarding the vibrational modes of phonons reflected by $\frac{\langle I^2 \rangle}{M\omega^2}$ term as exhibited in Fig. 2(a), a striking feature of the phonon band is that various optical phonon vibrational modes have differential degrees to participate in EPC corresponding to the same $\mathbf{q}$ -vector. The underlying causations behind this physical connotation can be revealed by the line width γ_{qv} representation. The γ_{qv} is primarily subjected to two factors: the nesting function $\xi(\mathbf{q})$ and the electron-phonon matrix element $g_{mn}(\mathbf{k}, \mathbf{q})$ based on the formula: $\gamma_{qv} = \pi\omega_{qv} \sum_{mn} \sum_{\mathbf{k}} |g_{mn}^v(\mathbf{k}, \mathbf{q})|^2 \delta(\varepsilon_{m,\mathbf{k}+\mathbf{q}} - \varepsilon_f) \times \delta(\varepsilon_{n,\mathbf{k}} - \varepsilon_f)$ [61]. Along Γ to Z $\mathbf{q}$ -route above 100 THz and at the F point of phonon band above 80 THz (see Fig. S2), we can evidently find the softening dips. The corresponding phonon dips are attributed to the main causation induced by FS nesting, which can be verified by the nesting function: $\xi(\mathbf{q}) = \frac{1}{N} \sum_{\mathbf{k}, i, j} \delta(\varepsilon_{\mathbf{k}, i} - \varepsilon_F) \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q}, j} - \varepsilon_F)$ in Fig. 2(b). Two relatively high peaks correspond to a strong

nesting strength along the Γ to Z q -route and at the F point. Next, we calculate the FS to check for nesting behavior. Of particular note is that two tripod-like FSs are buckled upside down to form nesting, evidenced in Fig. 2(d). This result explained that the softening dips on phonon modes caused by FS nesting. Moreover, the nature of the FS with differential Fermi velocity also affects the superconductivity. According to the relationship, $\xi(\mathbf{q}) \propto \oint \frac{d\mathbf{l}_k}{|\mathbf{V}_k \times \mathbf{V}_{k+\mathbf{q}}|}$, the Fermi velocities of $\mathbf{V}_k$ and $\mathbf{V}_{k+\mathbf{q}}$ at ε_F are almost reverse collinear, indicating the $\xi(\mathbf{q})$ is stronger at the nesting points [34]. Nesting at the mentioned points certainly affects the phonon frequencies, while the none-softening phonon frequencies corresponding to the same $\mathbf{q}$ -point contributing to EPC is interrelated with the $g_{mn}(\mathbf{k}, \mathbf{q})$, as reflected by the thickness of the line width in the phonon band [62]. Thus, the phonon softening caused by FS nesting and $g_{mn}(\mathbf{k}, \mathbf{q})$ are crucial factors causing a large T_c .

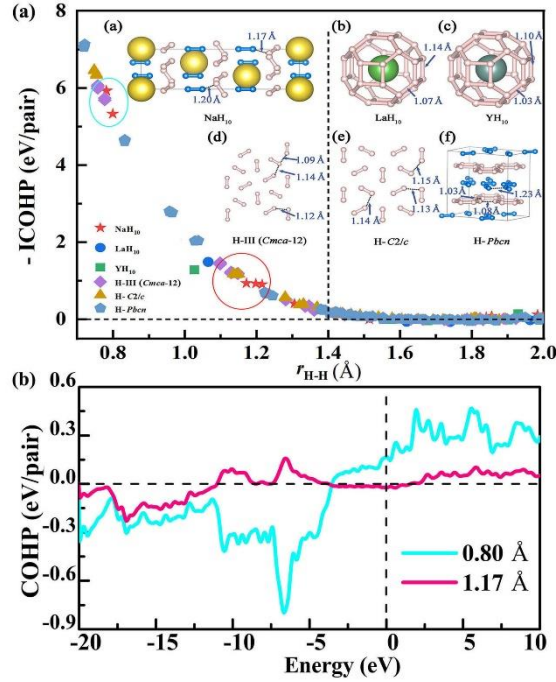


Fig. 3. (a) Calculated bond length r_{H-H} and the corresponding $-i\text{COHP}$ values between the nearest-neighbor H atoms in different system at 300 GPa. (b) Plot of COHP for H-H pairs separated by 0.80 Å (intramolecular distance) and 1.17 Å (intermolecular distance).

The properties of phonon band structures and energy band structures are closely related to the interactions between atoms, which, in turn, can be revealed by analyzing chemical bonds. We thus investigated the bonding characteristics of NaH₁₀ in comparison with clathrate-like hydrides LaH₁₀, YH₁₀ and insulating molecular phases of solid hydrogen at 300 GPa [63]. The bonding strengths were examined in-depth through calculating the $i\text{COHP}$ and COHP of H-H pairs [64]. As Fig. 3(a) illustrates, the bonding strengths between H₂-units of NaH₁₀ in solid red line region are less than the weak covalent bond strengths in extended clathrate hydrides LaH₁₀ and YH₁₀, and intramolecular bonding strengths in solid light-blue line region are approximate or slightly less than that in pure H-III phases. These results reconfirmed that the hydrogen framework is almost composed of molecular H₂-units. To explain the

abovementioned results, the COHP calculation in Fig. 3(b) indicated that the bonding molecular orbital (BMO, σ) of H_2 -molecule (0.80 Å) is completely occupied, and the antibonding molecular orbital (AMO, σ^*) is partially occupied due to the transferred electrons from sodium. Correspondingly, a small amount of electrons are distributed in the BMOs between H_2 -units, which ensure the charge connectivity between them resulting in metallicity.

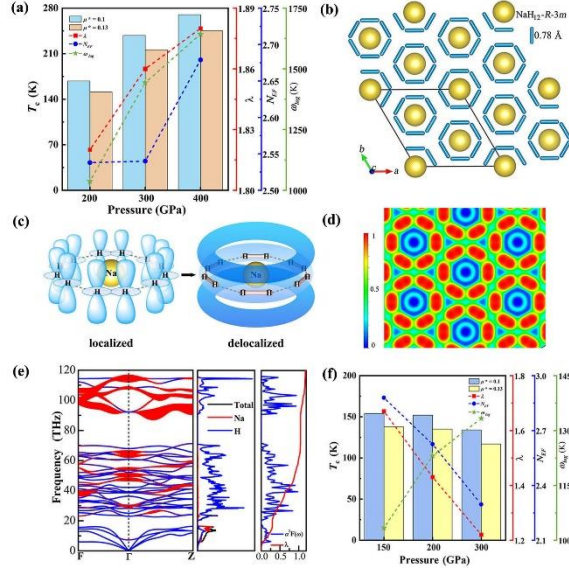


Fig. 4. (a) Calculated superconductivities for $R32\text{-NaH}_{10}$ as a function of pressures. (b) $R3m\text{-NaH}_{12}$ phase at 300 GPa, (c) Energy distribution spectra of localized and delocalized sp -hybridized electrons in the Lewis structure for planar benzene-like H_{12} sublattice. (d) ELF of $R3m\text{-NaH}_{12}$. (e) Phonon dispersion curves, $\alpha^2F(\omega)$, integral $\lambda(\omega)$, and (f) superconductivities for $R3m\text{-NaH}_{12}$ as a function of pressures.

To further understand the superconducting behavior of the H_2 -molecular-type NaH_{10} with pressure, we calculated T_c s, $\omega_{\log}$, λ and $N_{\mathcal{E}F}$ at different pressures in Fig. 4(a). The T_c s increase as pressures increases from 168 K at 200 GPa to 270 K at 400 GPa. As the $R32$ phase is compressed to 400 GPa, the moderate increase of T_c is mainly brought about by the enhanced EPC, $\omega_{\log}$ and $N_{\mathcal{E}F}$. And especially in medium-frequency vibration modes (25 to 80 THz), the peaks of the $\alpha^2F(\omega)$ have increased (see Fig. S2). Note that the influence of medium-frequency vibrational modes on the integrated EPC has further expanded by nearly 8%, reflecting electron-phonon matrix element driven by interatomic interactions contributes to λ continuously in a crucial manner. At 400 GPa, the abnormal performance of the optical phonon softening induced by FS nesting is increased at F point corresponding to > 80 THz, further enhanced EPC (see Fig. 2(b) and Fig. S2). Besides, $N_{\mathcal{E}F}$ increased with pressure enhancing the possibility of electrons being scattered by phonon, which increases the strength of EPC thus improves T_c . However, the effect of low-frequency modes on EPC become less significant with pressure, which suggests that T_c is so sensitive to the medium-frequency vibrational motions in this H_2 -molecular-type structure.

To propose more H_2 -molecule-type hydrides and investigate correlation between

molecular H₂-unit and high- T_c , we further doped sodium into the H-III phase for computational simulation at 300 GPa. Subsequently, we obtain a dynamically stable $R\text{-}3m\text{-NaH}_{12}$ structure in Fig. 4(b), which was in agreement with the previously predicted result in NaH₁₂ stoichiometry [30]. The molecular H₂-units with equal bond length of 0.78 Å shape into a planar benzene-like structure composed of 12-hydrogen atoms, but intermolecular interactions are also connected by non-covalent bonds and stacked along the c axis (see Fig. 4(d)). In sharp contrast to the insulating molecular phase H-III of solid hydrogen, $R\text{-}3m\text{-NaH}_{12}$ is metallic as determined by the background charges and electrons occupying the sp -hybridized antibonding bands, which form delocalized characteristics in planar benzene-like H₁₂-sublattice. This result is supported by comparing the kinetic energy relationship in the cases of “localized or delocalized electronic states” as discussed in Fig. 4(c) and Scheme S1. Next, we conducted superconductivity and illustrated the T_c of this newly designed phase at stability fields with the evolution of high pressure. The molecular-type hydride NaH₁₂ also has a notable T_c of 154 K at relatively low pressure of 150 GPa. Instructively, our discovery of new emergent of H₂-molecular-type hydrides with notable T_c highlights the correlation between H₂-units and novel superconductors.

In summary, we proposed a high-throughput structural search approach to screen H₂-molecular-type hydrides to quickly identify potential high- T_c . And confirmed new type pressure-induced near room-temperature superconductors in solely H₂-molecule constituted NaH₁₀ with T_c of 270 K at 400 GPa and NaH₁₂ with high- T_c of 154 K at 150 GPa, which is a first prototype in the family of H₂-molecular-type hydrides. Being subjected to extensive first-principles calculations, the electronic structures, bonding properties and superconductivities of NaH₁₀ and NaH₁₂ have been revealed. The potential near room-temperature superconductivity originates from strong EPC to scatter itinerant electrons. The unique delocalized background charges and electrons occupying the pressure-induced sp -hybridized antibonding bands of molecular H₂-units act as itinerant electrons to participate in EPC. Our work reshapes the cognition of hydrogen molecular dominated superconductivity and will stimulate future high-pressure experimental work on synthesis of these H₂-molecular-type structures to obtain room-temperature superconductors.

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Author Contribution

Z.L. and J.D.L contributed equally to this work. T.C. led the project. T.C., Y.H.L and Z.L conceived the project. Z.L, J.D.L, J.C.Y, S.Q.G, A.Z, and Q.Z. performed the calculations. Z.L., T.C. and E.Z. analysed the data and wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no conflict of interest.

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