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Molecular Hydride Superconductor BiH_4 with T_c up to 91 K at 170 GPa

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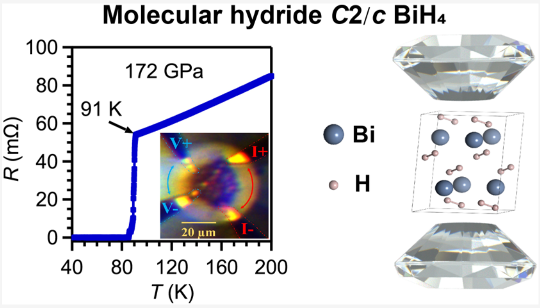
ABSTRACT: In pursuit of high-T_c hydride superconductors, the molecular hydrides have attracted less attention because the hydrogen quasimolecules are usually inactive for superconductivity. Here, we report on the successful synthesis of a novel bismuth hydride superconductor $C2/c$-BiH_4 at pressures around 170−180 GPa. Its structure comprises bismuth atoms and elongated hydrogen molecules with a H−H bond length of 0.81 Å at 170 GPa, characterizing it as a typical molecular hydride. Transport measurements revealed the occurrence of superconductivity with T_c up to 91 K at 170 GPa, as evidenced by a sharp drop of resistivity to zero and a characteristic downward shift of T_c under magnetic fields. Calculations by density functional theory elucidate that both midfrequency H-derived phonons and low-frequency vibrations from Bi atoms are important for the strong electron−phonon coupling in BiH_4, differentiating it from most high-T_c superconducting hydrides. Our work not only places $C2/c$-BiH_4 among the molecular hydride superconductors with the highest T_c but also offers new directions for designing and synthesizing more high-T_c hydride superconductors.



INTRODUCTION

At ambient pressure, hydrogen atoms tend to form stable two-atom molecules via the robust covalent bond with an energy of ~4.52 eV and a H−H distance of 0.74 Å.[1] As the lightest element in the periodic table, it has long been believed that, if the molecular hydrogen can be converted into atomic metallic hydrogen under high pressures, one should achieve high-temperature or even room-temperature superconductivity.[2−4] Thus, enduring efforts have been undertaken in the high-pressure community to obtain the metallic hydrogen via directly compressing molecular hydrogen.[5] This approach turns out to be an immense challenge due to the required exceptionally high pressures beyond the limits of current experimental capabilities. To overcome such obstacles, Ashcroft in 2004 proposed an alternative strategy of "chemical precompression" to metallize the hydrogen lattice of hydrogen-rich materials, namely, hydrides, under attainable pressure conditions.[6] This concept together with the advancement of theoretical structure predictions led to significant experimental breakthroughs in recent years in pursuit of high-T_c superconducting hydrides, which are predominantly centered on two categories,[7] i.e., the covalent hydrides as exemplified by SH_3,[8] and the clathrate-type hydrides represented by LaH_{10}[9,10] and CaH_6.[11,12] As shown in Figure 1, these two classes of high-T_c hydrides adopt three-dimensional hydrogen sublattices involving the dissociation of hydrogen molecules, which requires megabar pressure con-

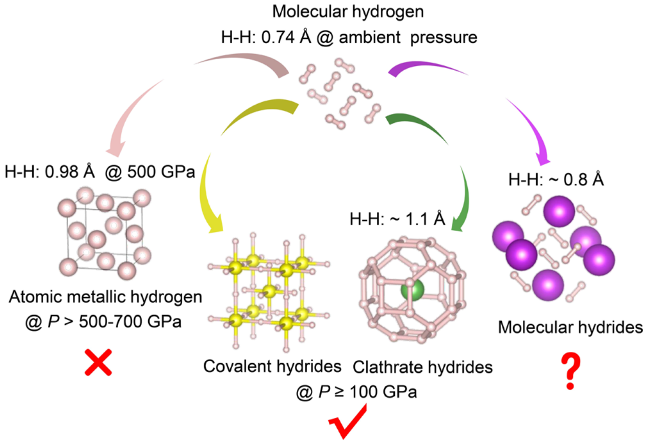


Figure 1. Possible routes to achieve metallic hydrogen with high-T_c superconductivity.

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ditions, i.e., 100−200 GPa. For the clathrate-type metal hydrides, the typical H−H bond length ∼1.1 Å is much longer than that of a hydrogen molecule.[13,14] Now, it is commonly believed that high-T_c superconductivity originates from the enhanced density of states near the Fermi surface $[N(E_F)]$ and electron−phonon coupling (EPC) of the metallic hydrogen sublattices in these hydrides.[15] Recent research has been focused on finding routes to reduce the stabilization pressures, for which the ternary or multinary hydrides have attracted much attention.[16]

In addition to the above approaches, the electron filling to the antibonding state of hydrogen molecules could be another approach to metallize hydrogen in the molecule-type hydrides, as illustrated in Figure 1. Recently, a series of molecular hydrides characterized by an exceptionally high hydrogen content, including LiH_6,[17] NaH_7,[18] BaH_{12},[19] and SrH_{22},[20] have been successfully synthesized in high-pressure experiments and preserved below megabar pressures. Although theoretical calculations have proposed a series of molecular hydrides with high-temperature superconductivity,[21−23] experimental observations of superconductivity in these systems remain rare, with some even exhibiting insulating behavior. This indicates futile charge transfer from the metal cations to the hydrogen molecules, which remain inactive to superconductivity. There are already some synthesized hydride superconductors that are considered to be of molecular type,[19,20] and among them with well-defined structures, BaH_{12} possesses the highest $T_c \approx 20$ K under 140 GPa.[19] Considering that the molecular hydrides generally display superior structural stability in comparison to the covalent and clathrate-type hydrides,[24] it is highly desirable to explore high-T_c superconductivity in the molecular hydrides via enhancing effective charge transfer. This holds the promise of significantly expanding the realm of hydride superconductor research and providing valuable insights for stabilization of hydride superconductors at lower pressures.[25] In this regard, the hydrides of heavy elements such as bismuth (Bi), the largest relative atomic mass among nonradioactive elements, are interesting since the high polarizability of their molecules tend to metallize at lower pressures.[26] By employing a theoretical prediction method to investigate the Bi−H system within the pressure range of 50−300 GPa, Ma et al. revealed a series of thermodynamically stable molecular hydride superconductors under high-pressure conditions.[27] Notably, BiH_4, BiH_5, and BiH_6 were predicted to have T_c around 100 K, offering a compelling material platform for experimental validation.

In this work, we successfully synthesized a new molecular hydride $C2/c$-BiH_4 under pressures around 170−180 GPa and temperatures around 2000 K. Its crystal structure is different from aforementioned theoretical predictions.[27] Transport measurement confirmed the occurrence of superconductivity with an optimal T_c of 91 K at 170 GPa, setting a new benchmark for the highest T_c observed among molecular hydride superconductors. In-depth analyses reveal a combination of ionic and covalent bonding between Bi and H_2-like molecular units in BiH_4, with both midfrequency H-derived phonons and low-frequency vibrations from Bi atoms primarily responsible for the enhanced EPC in BiH_4.

■ RESULTS AND DISCUSSION

Synthesis of Samples. We prepared a total of four diamond anvil cells (DACs) loaded with a combination of Bi foil and BH_3NH_3, which serves as the hydrogen source. Hereafter, we labeled the samples for resistance measurements as s1−s3, while that for X-ray diffraction (XRD) were labeled as s4. The XRD of s3 was also checked, as listed in Table S1. These samples were compressed to pressures between 170 and 180 GPa at room temperature, followed by laser heating to temperature ∼2000 K. Details about the sample preparation, structural, and transport measurements can be found in the Supporting Information.

Superconductivity. Figure 2a displays the temperature-dependent resistance $R(T)$ of s1 at 172 GPa, and the inset shows a photograph of the sample in DAC for resistance measurements. The $R(T)$ data clearly show a superconducting transition as evidenced by the sharp drop at 91 K, reaching zero resistance at ∼85 K. To ensure the reproducibility of the observed superconductivity and to determine the highest T_c, we conducted independent experiments on the s2 and s3, under similar conditions. The results are depicted in Figures S1−S3. It is noteworthy that the laser-heating process in some cases resulted in an incomplete reaction and the formation of competing phases. In addition, direct contact of electrodes occasionally occurred due to electrode deformation upon compression in DAC. As a result, the superconducting transitions in s2 and s3 failed to reach zero resistance. For the s2, we recorded $R(T)$ under different pressures from 189 to 138 GPa to follow the variation of T_c with pressure. The pressure dependence of T_c obtained from measurements on these samples is depicted in Figure 2b. In different experimental runs, T_c fluctuates slightly at pressures of 170−190 GPa, below which T_c gradually decreases with decreasing pressure, reaching about 78 K at 138 GPa for the s2. Upon further decompression, the diamond anvils were cracked.

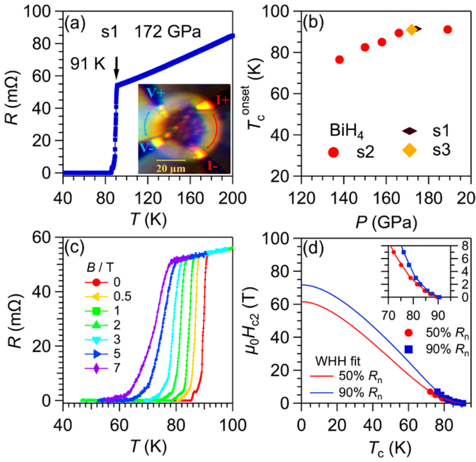

Figure 2. (a) Temperature-dependent resistance of s1 at 172 GPa upon the warming process with a sweep rate of about 0.4 K/min. The right insets show the configuration of the sample in the chamber and the permutation of electrodes. (b) Pressure dependence of the superconducting transition temperature in different runs. (c) Temperature dependence of resistance under various magnetic fields for s1 at 172 GPa. (d) Temperature dependence of $\mu_0H_{c2}(T)$ fitted by the WHH two-band model. The inset shows the details of $\mu_0H_{c2}(T)$ in the low field region.

The size of our bismuth hydride samples is relatively small, typically ranging from 30 to 40 μm in diameter, which makes it challenging to detect the diamagnetic effect within the current experimental capabilities.[28] Here, the occurrence of the superconducting transition was further corroborated by examining its response to the external magnetic fields. Figure 2c shows the $R(T)$ data of s1 under various magnetic fields. As can be seen, the superconducting transition is gradually suppressed with increasing magnetic fields, as expected. The values of T_c at 50%-R_n and 90%-R_n were utilized to establish the relationship between $\mu_0 H_{c2}(T)$ and temperature. As shown in Figure 2d, within the magnetic field range of 0−7 T, $\mu_0 H_{c2}(T)$ exhibited a distinct nonlinear behavior, characterized by a prominent upward trend, commonly observed in two-band superconductors. Thus, we fit the experimental $\mu_0 H_{c2}(T)$ data with a Werthamer−Helfand−Hohenberg (WHH) two-band model[29] in the dirty limit, yielding a zero-temperature $\mu_0 H_{c2}(0)$ = 61.5 T for $T_c^{50\%Rn}$ and 71.7 T for $T_c^{90\%Rn}$, respectively. These values are much smaller than the weak-coupling Pauli limit of $\mu_0 H_p^{BCS} = 1.84 T_c \approx$ 165.0 and 166.5 T. Details of fitting are provided in the Supporting Information. Thus, our above transport measurements established the successful synthesis of a superconducting bismuth hydride with an optimal T_c = 91 K at about 170 GPa.

Structural Analysis. Previous theoretical calculations on the Bi−H system have predicted several molecular hydride superconductors with estimated T_cs reaching around 100 K under high pressures.[27] To determine the crystal structure of the superconducting bismuth hydride obtained in this work, we performed in situ XRD measurements on the s4 synthesized at 170 GPa. Figure 3a presents the representative XRD pattern, in which strong diffraction spots indicated the good crystallinity of the synthesized sample. By comparison of the acquired XRD data with the Bragg positions of the cubic phase of bismuth, it was evident that bismuth metal had undergone a complete reaction with the hydrogen released from the decomposition of NH_3BH_3. However, the XRD pattern of s4 at 170 GPa cannot be indexed by any structures of the Bi−H phases predicted in a previous theoretical study.[27] Therefore, we resorted to the CALYPSO structure search method by conducting a comparison and search based on the obtained XRD pattern.[30−32] Details of the structure search process are comprehensively listed in the Supporting Information. The results reveal that the diffraction peaks matched the BiH_4 phase with the space group $C2/c$. As illustrated in Figure 3a, Rietveld refinement with the $C2/c$-BiH_4 structural model achieves an excellent fitting result, and the obtained lattice parameters and unit cell volume are listed in Table S2. As illustrated in Figure 3b, XRD patterns of s4 collected upon decompression down to 130 GPa remain the same and do not show any peak splitting or appearance of new diffractions. This confirmed that the $C2/c$-BiH_4 synthesized at 170 GPa remains stable down to at least 130 GPa, below which our diamond anvils were cracked during the depressurization. Comparison of the XRD pattern of s4 at 170 GPa with that of s3 at 171 GPa, Figure S4, confirmed that the superconducting sample indeed corresponds to the $C2/c$-BiH_4. The calculated equation of state (EOS) showed excellent agreement with the experimental P−V data in Figure 3c, further ascertaining the stoichiometric ratio of structural model $C2/c$-BiH_4 shown in Figure 3d.

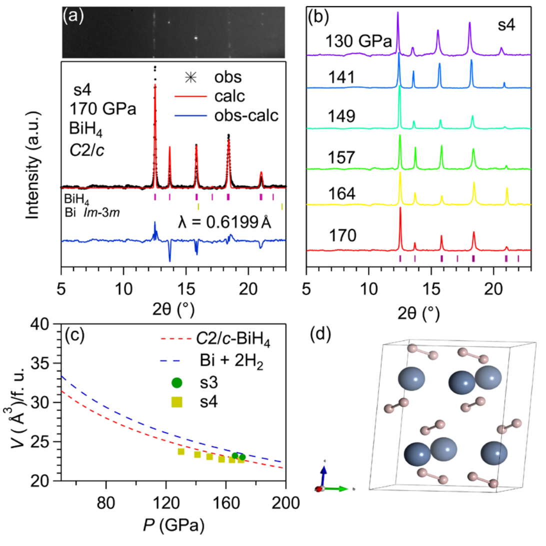

Figure 3. (a) XRD pattern and the result of Rietveld refinement for BiH_4 at 170 GPa in the $C2/c$ structure. Black stars: experimental data; red line: simulated XRD based on the structural model; purple vertical lines: Bragg diffraction positions of the structure; blue line: difference between the simulated and the original XRD. The upper panel shows the XRD image of corresponding powder XRD pattern with the incident X-ray wavelength of 0.6199 Å. (b) Representative integrated XRD patterns of BiH_4 upon decompression from 170 to 130 GPa. (c) Experimentally obtained volume per formula unit for BiH_4 plotted as a function of pressure. Green circles and yellow solid squares represent the experimental data for s3 and s4, respectively. Theoretical EOS of BiH_4 is plotted as red dashed line. Blue dashed lines represent ideal mixtures of Bi+2H_2. (d) Crystal structure model of $C2/c$-BiH_4. Blue and pink spheres represent bismuth and hydrogen atoms, respectively.

As shown in Figure 3d, the theoretically calculated hydrogen sublattice of $C2/c$-BiH_4 consists of H_2-like molecular units with the H−H bond length of 0.81 Å at 170 GPa, and the calculated structural parameters are listed in Table S3. The bond length is slightly elongated compared to that of a hydrogen molecule (0.74 Å) at ambient pressure,[1] but it is much shorter than those in monatomic hydrogen (0.98 Å) at 500 GPa[4] and the clathrate hydrides (e.g., ∼1.1 Å for LaH_{10} at ∼170 GPa).[13,14] The shortest H−H distances in typical hydride superconductors are given in Table S4. The previous theoretical studies suggested that $Pmmn$-BiH_4 stood as the lowest enthalpy phase possessing this stoichiometric ratio within the 130−200 GPa range.[27] We then conducted enthalpy calculations incorporating zero-point vibrational energy (ZPE) for these two structures shown in Figure S6 and found that the $C2/c$-BiH_4 exhibits a little higher enthalpy of 12 meV/atom than that of $Pmmn$-BiH_4 at around 170 GPa. Considering that the DFT calculations were conducted at 0 K, temperature-induced effects might favor the stabilization of $C2/c$-BiH_4 under experimental conditions. In addition, both $C2/c$-BiH_4 and $Pmmn$-BiH_4 belong to molecular hydrides, exhibiting similar structural motifs but slight differences in the intra- and intermolecular H−H bond length at the same pressure, emphasizing the inclination of Bi atoms to form molecular hydrides across diverse structural configurations within bismuth hydrides.

Theoretical Analysis. The bonding nature of $C2/c$-BiH_4 was explored through electron localization function (ELF) and Bader charge analysis. As shown in Figure 4a, the ELF value is approximately 0.96 between the H−H atoms, which confirms the presence of H_2-like molecular units. Besides, the ELF value (∼0.5) between Bi and H atoms is much lower, while it is still higher than that between metal and H atoms in other molecular hydrides such as BaH_{12},[19] indicating weak but discernible Bi−H bonding. Bader charge analysis reveals an effective charge transfer of approximately 0.665e per Bi atom from Bi to H. To gain further insights into the bonding behavior, we employed a crystal orbital Hamilton population (COHP) analysis to quantify interatomic interactions. Table S5 and Figure S7 present the integrated COHP (ICOHP) up to the Fermi level

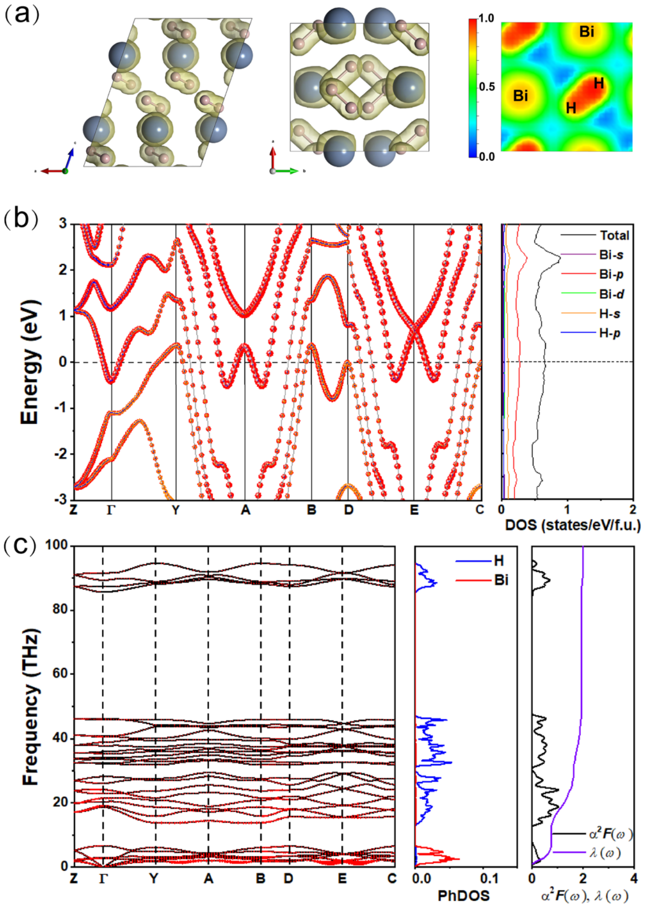

Figure 4. (a) 3D-electron localization function (ELF) with an isosurface value of 0.75 and ELF projected on the plane (001) of BiH_4. (b) Calculated electronic band structure and projected DOS of BiH_4 at 170 GPa. (c) Calculated phonon dispersion, projected phonon density of states, Eliashberg phonon spectral function $\alpha^2F(\omega)$, and integrated electron−phonon coupling $\lambda(\omega)$ for $C2/c$-BiH_4 at 170 GPa.

and negative projected COHP (−pCOHP) data for Bi−H and intra- and intermolecular H−H interactions. The observed strong intramolecular and weak intermolecular H−H interactions indicate the characters of molecular hydrides (Table S5). Besides, the intramolecular H−H bonds exhibit an antibonding character by negative −pCOHP at the Fermi level, which supports electron transfer from Bi atoms to the H_2-like molecular units filling the antibonding orbitals (Figure S7). Moreover, we identified the discernible Bi−H interaction supported by the ICOHP values along with −pCOHP values of Bi−H interactions around the Fermi level, indicating weak covalent bonding between Bi atoms and H_2-like molecular units. Therefore, the Bi−H interaction is characterized as a mixture of ionic and covalent bonds, similar to the bonding nature between the Ce atoms and H_{29} cages in clathrate hydride CeH_9.[33] Different from the other molecular hydrides, such a novel Bi−H interaction could play an important role in enhancing the coupling between metal atoms and H_2-like molecules.

It is quite encouraging to achieve a relatively high T_c of 91 K in molecular hydride BiH_4. To gain deeper insights into the superconducting behavior of $C2/c$-BiH_4, we have undertaken theoretical calculations on its electronic and phonon band structures. The band structure and density of states (DOS) of BiH_4 displayed in Figure 4b reveal its metallic nature. The $N(E_F)$ primarily originates from Bi-6*p* orbitals, while the contribution of hydrogen electrons is relatively small (∼19%), as shown in Figure S8, as a consequence of the H_2-like molecular units. Then, we conducted the analysis of phonon DOS, Eliashberg phonon spectral function $\alpha^2F(\omega)$, and EPC constant $\lambda(\omega)$. As shown in Figure 4c, the absence of an imaginary frequency in the phonon spectra of BiH_4 at 170 GPa indicates its dynamical stability. The calculated phonon DOS can be separated into three regions: the low-frequency vibrations from Bi atoms and the mid- and high-frequency vibrations from hydrogen atoms. The calculated EPC parameters λ for BiH_4 at 170 GPa is 2.01, which is comparable to those well-known high-T_c superconductor such as SH_3[34] and LaH_{10}.[13,14] The low-frequency translational vibrations from the Bi atoms (below 9 THz) contribute 38% of the total λ, while the 59% of the total λ originates from the midfrequency bending vibrations from hydrogen (16−48 THz). These results highlight that mid-frequency H-derived phonons and low-frequency vibrations from Bi atoms are mainly responsible for the EPC in BiH_4. In contrast, the high-frequency H-stretching vibrations make a dominant contribution to the overall EPC in covalent and clathrate-type hydride systems.[13,14,34] The contribution of Bi atoms to the EPC in BiH_4 was also compared with the superconducting properties of elemental bismuth. As the heaviest nonradioactive element, Bi is notable for its high λ values in various superconducting allotropes. For instance, the Bi−III phase exhibits a T_c of 7 K at 3 GPa with a relatively high EPC constant ($\lambda \sim 2.75$).[35] However, due to the significantly high atomic mass of bismuth, coupling its electrons with high-frequency phonons in pure bismuth remains challenging. While in BiH_4, the λ is slightly lower than that in the Bi−III phase, the logarithmic average phonon frequency ($\omega_{\log}$) is significantly enhanced. This enhancement is primarily attributed to the incorporation of H_2 molecular units, with midfrequency H-derived phonons—arising from weak bonding and charge transfer between Bi and H—playing a crucial role in modulating T_c. The superconducting T_c of the predicted stable H-rich compounds is evaluated through the Migdal−Eliashberg equations.[36] As a result, the estimated T_c for BiH_4 is 88−125 K (for μ^* of 0.1−0.25) at 170 GPa shown in Figure S9. We further calculated the T_c values at higher pressures. As shown in Figure S11, the variation of T_c in the 170−250 GPa range indicates that T_c remains relatively constant between 170 and 225 GPa and begins to decline beyond 225 GPa. It forms a dome-like T_c-P phase diagram similar to those observed in other hydride superconductors.[9−12]

The observed optimal T_c of 91 K at 170 GPa places $C2/c$-BiH_4 as a new benchmark of the highest T_c values among molecular hydride superconductors. Here, the chemical precompression of hydrogen in the BiH_4 achieves the equivalent of a metallic molecular phase of hydrogen via electron transfer without breaking the quasi-molecular units, clearly at much lower pressures than in pure hydrogen itself. In contrast, high-T_c superconductivity in LaH_{10}[9,10] and CaH_6[11,12] was achieved via breaking the quasi-molecular units upon electron doping and converting them into cage-like structures. Moreover, it has been generally recognized that the quasi-molecular hydrogen units (e.g., H_2, H_3) in the structures of hydrides have negligible contribution to superconductivity because the corresponding bonding states are located well below the Fermi level. In comparison to other experimentally synthesized molecular hydrides like BaH_{12}[19] and SrH_{22},[20] the $C2/c$-BiH_4 contains only molecular hydrogen motif, and it is the unique mixing of ionic and weak covalent bonding between bismuth and molecular hydrogens that enables considerable electron transfer and enhances the contribution of Bi atoms and midfrequency H-derived phonons to the EPC from both heavy bismuth atoms and light hydrogen atoms, both factors contributing to a relatively high T_c over 90 K. Hence, the unique bonding between Bi atoms and H_2-like molecular units is proved feasible in the realization of high-T_c superconductivity, which should represent a new strategy and thus open a new avenue in the field of hydride superconductors. This undoubtedly refreshes the understanding toward hydrogen-molecule motifs in superconducting hydrides and emphasizes that not only should we consider the light-element networks but also pay attention to the importance of host atoms in quest for high-T_c superconductors.

■ CONCLUSIONS

In summary, we have successfully synthesized a novel molecular bismuth hydride superconductor $C2/c$-BiH_4 with an optimal T_c of 91 K at ∼170 GPa, which is the highest T_c value among existing molecular hydrides. Detailed analyses revealed the mixing of weak covalent and ionic bonding between Bi and the H_2 molecules and thus enhanced EPC responsible for the observed high T_c in BiH_4. Our work not only expands the range of experimentally synthesized high-temperature superconducting hydride structures but also underscores the capability of molecular hydrides to achieve high-temperature superconductivity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c15137.

Experimental methods, computational details, structural information, and electron and phonon properties of bismuth hydrides (PDF)

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Notes

The authors declare no competing financial interest.

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