

Synthesis of hafnium superhydrides at megabar pressures

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Recent theories have predicted the existence of another class of hafnium superhydride $P6_3/mmc\text{-HfH}_{10}$ with a two-dimensional layered structure and remarkable high- T_c around 213–234 K at 250 GPa. Its structure contains a planar pentagraphenelike hydrogen sublattice, which does not resemble the discovered high- T_c superconductors of covalent-bonded hydrogen structure of H_3S and clathrate-type structure of LaH_{10} . Here, we present the synthesis of hafnium superhydrides by the direct chemical reaction of Hf and H_2 or with ammonia borane as the hydrogen source in laser-heated diamond anvil cells ranging from 200 to 302 GPa. Synchrotron x-ray diffraction data reveal the presence of previously predicted $Pm\bar{3}n\text{-HfH}_3$, $Fddd\text{-HfH}_4$, and $C2/m\text{-HfH}_{14}$ phases, and a unique triclinic phase $P\bar{1}\text{-HfH}_{10.5}$ was identified. Unfortunately, no existence of the $P6_3/mmc\text{-HfH}_{10}$ phase was detected in the studied pressure range. Electrical resistance measurements demonstrate the synthesized products exhibiting good metallic character and absence of superconductivity down to ~ 80 K. Theoretical calculations reveal the presence of the atomic H and H_2 molecular units within the structure of $P\bar{1}\text{-HfH}_{10.5}$, which is mainly responsible for the low superconducting temperature.

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I. INTRODUCTION

Searching for room-temperature superconductors is one of the most challenging tasks in condensed matter physics and materials science. Based on the Bardeen-Cooper-Schrieffer (BCS) theory, a high Debye temperature and strong electron-phonon coupling (EPC) are necessary for obtaining high superconducting temperature T_c , hence metallic hydrogen is a good candidate for achieving such a goal [1]. However, metallization of the hydrogen requires ultrahigh pressure of ~ 500 GPa, which is still technically challenging in diamond anvil cells (DACs) [2–4]. For these reasons, chemical precompression with certain elements in hydrogen-dominant compounds could lower the metallization pressure, and facilitates the synthesis of the high- T_c superconductors under experimentally accessible conditions [5].

Based on the BCS phonon-mediated theory, the compressed H_3S was experimentally discovered to display a critical temperature of 203 K at 150 GPa in 2015 [6], and this finding stimulated several studies to seek high- T_c superconductivity in binary and ternary superhydrides [7–14]. Recently, room temperature (RT) superconductivity with a critical temperature of 288 K at 267 GPa was reported in a ternary carbonaceous sulfur hydride—this observation is controversial and neither the chemical composition nor crystal structure was identified [15–18]. The synthesized H_3S has a three-dimensional S-H covalent bond network with cubic $Im\bar{3}m$ symmetry, in which S atoms form a body-centered cubic lattice [19–22]. Later, another family of binary superhydrides with clathratelike structures were predicted and successfully synthesized, which was proposed in CaH_6 and can be viewed as metal-doped metallic hydrogen [23]. For example, LaH_{10} exhibits near room temperature superconductivity with T_c of 250–260 K [24,25]. Other superhydrides, including $Im\bar{3}m\text{-CaH}_6$ [26,27], $Im\bar{3}m\text{-YH}_6$ [28], and $P6_3/mmc\text{-YH}_9$ [29,30], $P6_3/mmc\text{-CeH}_9$ [31,32] and $Fm\bar{3}m\text{-CeH}_{10}$ [33], $P6_3/mmc\text{-ThH}_9$ and $Fm\bar{3}m\text{-ThH}_{10}$ [34] with superconducting temperature T_c above 100 K were also prepared in diamond anvil cells. While, hydrogen-rich compounds $P6_3/mmc\text{-}F\bar{4}3m\text{-PrH}_9$ [35], and $P6_3/mmc\text{-NdH}_9$ [36] with similar clathrate structures demonstrate low superconducting transition below 10 K. Theoretical calculations reveal that the presence of magnetic order within those

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superhydrides is likely responsible for their low superconducting temperatures [35,36]. In the structures of all these compounds, the hydrogen atoms generate a cage-like network and metal elements occupy the centers of the hydrogen cages [10,37,38].

In 2020, a layered hafnium decahydride $P6_3/mmc$ -HfH₁₀ with high- T_c of $\sim 213 - 234$ K at 250 GPa was predicted in the Hf-H system [39]. Unlike the LaH₁₀, where H atoms form H₃₂ cages within the three-dimensional clathrate structure, $P6_3/mmc$ -HfH₁₀ possess pentagraphenelike with three planar H₅ pentagons, and Hf atoms reside in the same plane with these pentagons. A metastable $P6_3/m$ -HfH₉ with unique hydrogen tubes is predicted and its calculated superconducting temperature of ~ 110 K at 200 GPa, arising from the electron-phonon coupling of the H₁₂ tube and HfH₃ framework within its crystal structure [40]. The clathrate structure of $Im\bar{3}m$ -HfH₆ is proposed to have a maximum T_c of 132 K at 600 GPa [41]. Other stable hafnium hydride phases, e.g., $C2/m$ -HfH₁₄, $P\bar{1}$ -HfH₁₀, $Cmc2_1$ -HfH₆, $Fddd$ -HfH₄, and $Pm\bar{3}n$ -HfH₃, contain in their structures atomic hydrogen, diatomic H₂-like molecules, or triangular H₃ units leading to weak electron-phonon coupling and low magnitude of the density of states at the Fermi level, and hence low superconducting temperature T_c [39,42]. However, the Hf-H system was rarely investigated experimentally at high pressures. Low stoichiometric hydrides, e.g., $Pm\bar{3}n$ -HfH₃ and $I\bar{4}3d$ -Hf₄H₁₅, were experimentally synthesized from the hafnium metal with excess hydrogen or dihydride HfH₂ with hydrogen below 40 GPa [43]. Electrical resistivity measurements of Hf₄H₁₅ reveal the superconducting temperature is ~ 4.5 K at 23 GPa [43]. In 2022, Zhang *et al.* observed the superconducting temperature of ~ 83 K at 243 GPa in hafnium hydride, and x-ray analysis indicated the superconducting phase is $C2/m$ -HfH₁₄ [44]. No other hydrogen-contained compounds have been reported experimentally in the Hf-H system, especially at megabar pressures.

In this work, we present the synthesis of the Hf superhydrides from the hafnium metal and hydrogen or ammonia borane (AB) in laser-heated diamond anvil cells. With the aim to synthesize the high- T_c superconductor $P6_3/mmc$ -HfH₁₀ as predicted in recent theories, we examined the Hf-H system above 200 GPa and we did not find the existence of $P6_3/mmc$ -HfH₁₀. Instead, another compound $P\bar{1}$ -HfH_{10.5} that contains atomic H and H₂ molecular units was successfully synthesized. This compound displays good metallic features, and no signature of superconductivity was observed down to 80 K. Theoretical calculations reveal that the emergence of low estimated- T_c (< 80 K) of the $P\bar{1}$ -HfH_{10.5} phase, which mainly arises from the weak electron-phonon coupling and low contributions of the H atoms to the total density of states at the Fermi level.

II. EXPERIMENTAL AND THEORETICAL METHODS

A. Synthesis of hafnium superhydrides at megabar pressures

High pressure synthesis of hafnium superhydrides was performed in customized DACs. The diamonds used in DACs have a culet size of $\sim 20 - 25$ μm and were beveled at 8.0° to a diameter of $\sim 250 - 300$ μm . To avoid the failure of the

diamond at megabar pressures, especially during the laser heating (hot hydrogen easily diffuses into the surface of the culet if defects are present), rigorous polishing and etching were carried out. A metallic T301 stainless steel was laser cut through the whole preindented part and mixtures of epoxy and CaO, MgO, or *c*-BN were used as the insulating materials for both the x-ray diffraction (XRD) experiments and electrical resistance measurements. For electrical resistance measurements, four tungsten electrodes covered with gold with thicknesses of ~ 200 nm with van der Pauw geometry were deposited onto the surface of the one-side anvils [see Fig. 4(a) for scheme of the typical arrangement of the insulating gasket].

The typical size of hafnium (99.5%, Alfa Aesar) is ~ 2 μm thick and $\sim 10 - 15$ μm diameter. Pure hydrogen (99.999%) or ammonia borane (NH₃BH₃, AB, 97%, Sigma Aldrich) was used as the hydrogen source. All the sample loadings were performed in an argon-filled glove box with a level of H₂O and O₂ below 0.1 ppm. The pressure of the DACs was increased to about 3.0 GPa in the glove box for trapping hydrogen (~ 10 GPa for AB loading) and the DACs were taken out from the glove box and compressed to the desired pressures. Pressure in DACs was calibrated using the diamond edge pressure scale [45,46] or the Raman vibron of the hydrogen if the corresponding Raman spectra were detectable [2]. All six DACs prepared and studied in the present work are summarized in Table S1.

Synchrotron x-ray data were mainly collected at Beamline P02.2 at PETRA III, Deutsches Elektronen-Synchrotron (DESY) using a beam spot size of $\sim 2 \times 2$ μm^2 and a 2D area Perkin Elmer XRD 1621 detector ($\lambda = 0.2885$ Å). One side of the DAC was heated to ~ 2200 K with the aid of a pulsed YAG laser. The diffraction images generally were recorded before and after laser heating to check the XRD pattern changes. Moreover, to examine the distribution and homogeneity of the synthesized hafnium hydrides and estimate the pressure gradient around the synthesized sample [from the equation of state (EoS) of insulating material MgO or CaO], we collected the x-ray powder diffraction data from the spatial area of 100×100 μm^2 with a step of 10 μm within the horizontal and vertical directions. The x-ray data of cell No. 4 were collected at 13-IDB at GeoSoilEnviroCARS, Advanced Photon Source (APS), Argonne National Laboratory ($\lambda = 0.2952$ Å, a beam spot size of $\sim 2.5 \times 3.5$ μm^2 , Pilatus 1M CdTe detector). All diffraction images were integrated using DIOPTAS software [47], x-ray patterns were fitted by the Le Bail method using the GSAS-EXPGUI package [48], and the predicted structures of $Pm\bar{3}n$ -HfH₃, $Fddd$ -HfH₄, $C2/m$ -HfH₁₄, and $P\bar{1}$ -HfH_{10.5} were used as the starting models to carry out all the data refinements.

B. High pressure electrical transport measurements

Electrical resistance measurements were conducted on cell No. 3 using the four-probe technique in the range of 80–300 K to investigate the possible high T_c of the synthesized samples. All measurements were performed with the currents in the range of 100–200 μA (Keithley 6220 current source and 2000 multimeter). The experimental data were recorded upon warming since it yields a more stable temperature reading.

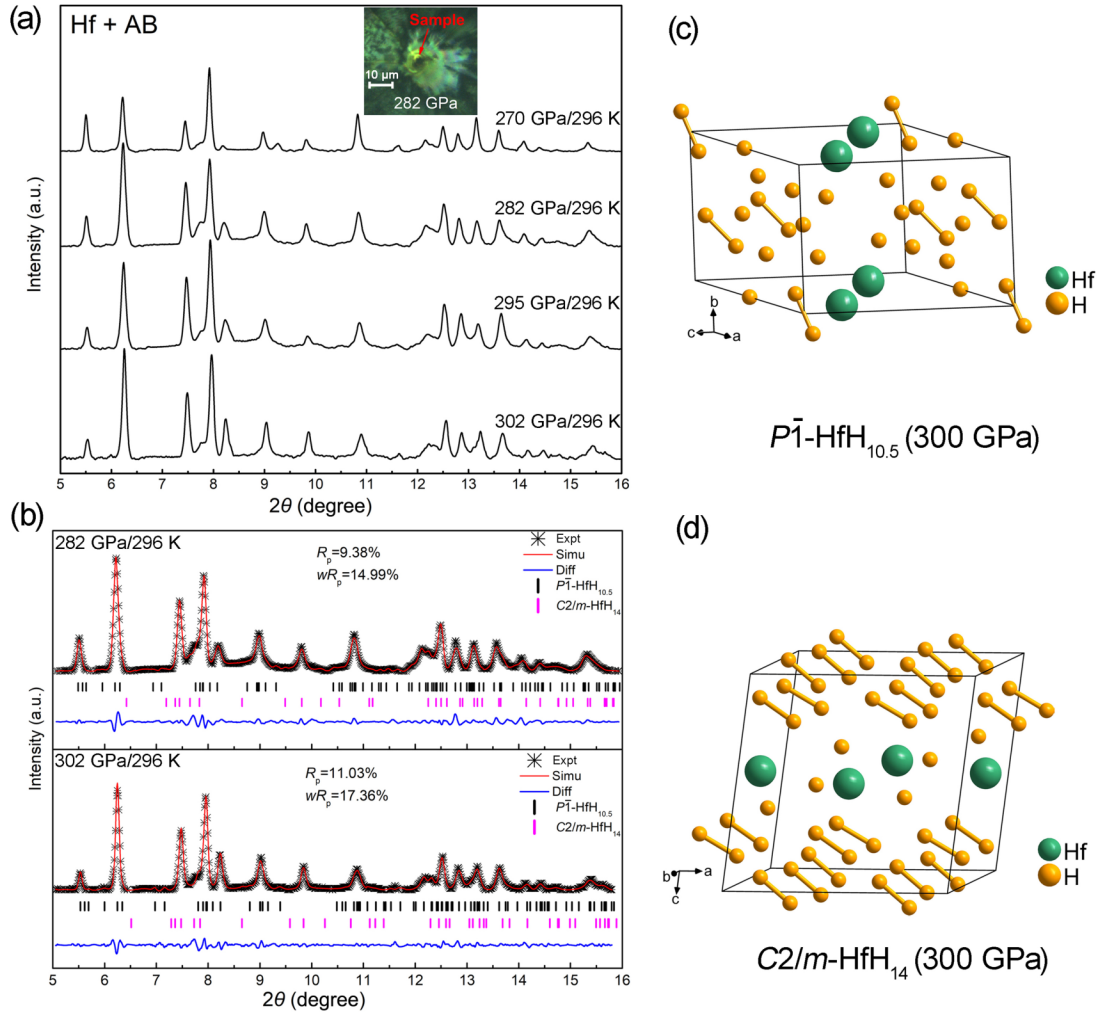


FIG. 1. (a) Powder XRD patterns of $P\bar{1}$ -HfH_{10.5} and C2/m-HfH₁₄ superhydrides synthesized from Hf metal and AB at ~ 270 GPa/2200 K (cell No. 1, $\lambda = 0.2885$ Å). Experimental diffraction data were collected at 270 GPa 296 K and pressure was isothermally increased to 302 GPa at RT (296 K). (b) Le Bail fit of the representative x-ray data of hafnium superhydrides at 282 and 302 GPa/296 K. The black asterisks, red solid line, and blue curves represent the measured scattering intensity, the fit to the data, and difference profiles. The fitted R values are indicated in the relative pressures. The crystal structures of (c) $P\bar{1}$ -HfH_{10.5} and (d) C2/m-HfH₁₄ at 300 GPa.

The temperature was measured with an accuracy of ~ 1.0 K by a silicone diode thermometer (Lakeshore DT-470) attached to the DAC body. Electrical resistance data were collected at 216 GPa (after Hf + H₂ was kept for one month at room temperature, before laser heating), 220 GPa (after laser heated at ~ 2200 K), and 235 GPa (after XRD data were collected at DESY).

C. Theoretical calculations

We employed the swarm-intelligence-based CALYPSO [49,50] x-ray diffraction data assisted structural prediction method for the investigation of HfH_{*n*} ($n = 9.5, 10$, and 10.5) compounds at 300 GPa, where 1000 $\sim$ 1200 structures were investigated for each stoichiometry to ensure the convergence of our structure searches. The underlying energetic calculations were performed with the plane-wave pseudopotential method as implemented in the VASP code [51]. The Perdew-Burke-Ernzerhof generalized gradient approximation [52,53] was chosen for the exchange-correlation functional. The

electron-ion interaction is described by projector augmented-wave [54] potentials with 12 and 1 valence electrons for Hf and H atoms, respectively. A kinetic cutoff energy of 700 eV and Monkhorst-Pack k meshes with grid spacing of 0.25 Å⁻¹ were adopted to ensure the enthalpy converges to better than 1 meV/atom. The phonon spectrum and EPC of $P\bar{1}$ -HfH_{10.5} were calculated within the framework of linear response theory through the Quantum ESPRESSO code [55] where ultrasoft pseudopotentials [56] were used with a kinetic energy cutoff for wave functions of 80 Ry and a kinetic energy cutoff for charge density and potential of 1000 Ry. $4 \times 4 \times 2$ q meshes and $16 \times 16 \times 8$ k meshes were used for $P\bar{1}$ -HfH_{10.5} to compute the EPC matrix elements. EPC constant λ , $\omega_{\log}$, and T_c were solved using the AD-McMillan equation [57].

III. RESULTS AND DISCUSSION

To investigate the formation of Hf superhydride superconductors with high T_c , we successfully loaded six diamond

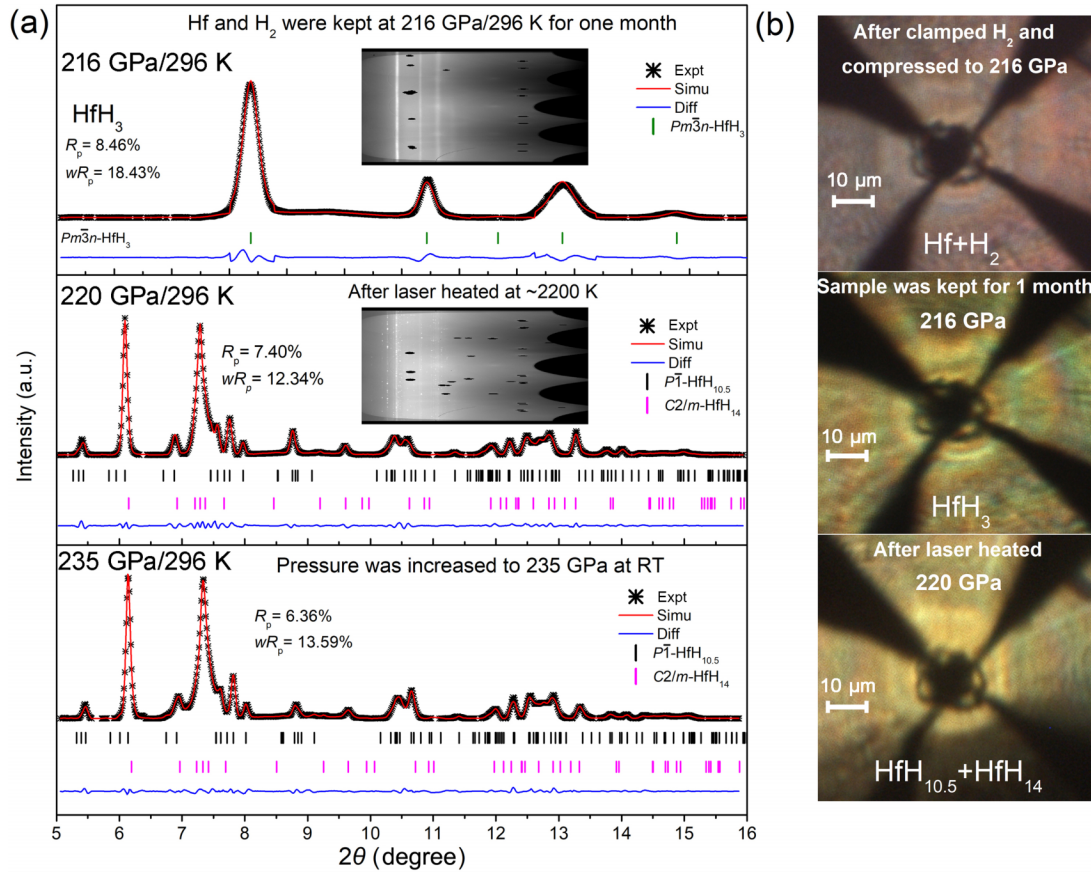


FIG. 2. (a) X-ray diffraction patterns of synthesized hafnium superhydrides in cell No. 3 using Hf metal and H_2 as the starting reactants ($\lambda = 0.2885$ Å). Le Bail fit of these x-ray data collected before and after laser heating at 216, 220, and 235 GPa/296 K. The black asterisks and red solid line represent the measured scattering intensity and the fit to the data. The vertical bars indicate Bragg reflection positions in two phases together with difference profiles (blue lines) shown at the bottom. The diffraction images and fitted R values are indicated in the relative panels. (b) Images of the sample after clamped hydrogen and increased to 216 GPa at RT (top). The sample was kept for 1 month at RT, pressure was increased to 216 GPa (middle), and sample was laser heated at ~ 2200 K (bottom). Cell No. 3 was prepared with a van der Pauw method for electrical resistance measurements.

anvil cells (DAC cells No. 1–6) with Hf and H_2 or using AB as the hydrogen source above 200 GPa. We initially loaded a ~ 2 - μm -thick Hf sample together with AB polycrystalline in a 20- μm -diameter culet DAC in an argon-filled glove box (cell No. 1) to check the existence of the $P6_3/mmc\text{-HfH}_{10}$ above two megabars. AB proved to be one of the best hydrogen sources in previous experiments with the reaction path of $\text{Hf} + \text{NH}_3\text{BH}_3 \rightarrow \text{HfH}_x + c\text{-BN}$ if heating is employed [22,36]. Pressure was directly increased to 270 GPa after the Hf and AB were loaded at RT. Synchrotron powder XRD data were collected at DESY. As shown in Fig. 1, new XRD peaks appeared after the sample was laser heated at ~ 2200 K, and we found the diffraction patterns could not be fitted by the previously predicted $P6_3/mmc\text{-HfH}_{10}$ or $P\bar{1}\text{-HfH}_{10}$ (see Fig. S1 [58]). Therefore, we used CALYPSO code to perform the crystal structure search for HfH_n ($n = 9.5, 10$, and 10.5) compounds at 300 GPa. According to the calculations, we found a unique compound triclinic $P\bar{1}\text{-HfH}_{10.5}$ ($Z = 2$), which remains dynamically stable in the range of 170 to 300 GPa.

We tried to perform x-ray data refinements from different predicted phases of hafnium hydrides: the XRD patterns of the synthesized compound finally can be indexed as the

mixed phase of $P\bar{1}\text{-HfH}_{10.5}$ and $C2/m\text{-HfH}_{14}$. Quantitative phase analysis using Rietveld refinements is inapplicable to our XRD data, hence we estimated their phase fractions based on the relative intensities of their main diffraction peaks [59,60]. The calculated fractions at 282 GPa are $73.4\% \pm 6.4\%$ and $26.6\% \pm 6.4\%$ for $P\bar{1}\text{-HfH}_{10.5}$ and $C2/m\text{-HfH}_{14}$, respectively [large error bars arising from the diffraction peaks overlapping, see Fig. 1(a) and Table S1]. Our observations here are quite different from the recent report of Zhang *et al.*, in which there are no diffraction peaks that appear below 2θ angle of 7° and some of the diffraction peaks are unidentified around 8° [44]. The refined lattice parameters at 302 GPa are $a = 2.9884(5)$ Å, $b = 3.0358(8)$ Å, $c = 5.6889(14)$ Å, $\alpha = 76.01(2)^\circ$, $\beta = 89.19(2)^\circ$, $\gamma = 90.79(2)^\circ$, and $V = 50.07(1)$ Å³ for $P\bar{1}\text{-HfH}_{10.5}$; and $a = 4.4923(2)$ Å, $b = 3.0988(11)$ Å, $c = 4.4584(7)$ Å, $\beta = 97.42(2)^\circ$, and $V = 61.55(4)$ Å³ for $C2/m\text{-HfH}_{14}$. The volume of the obtained data agrees well with our theoretical predictions ($V = 50.66$ Å³ at 300 GPa, see Tables S2 and S3 [58]). Unlike the hexagonal $P6_3/mmc\text{-HfH}_{10}$, the crystal structure of $P\bar{1}\text{-HfH}_{10.5}$ resembles the low- T_c phase $P\bar{1}\text{-HfH}_{10}$, both containing diatomic H_2 unit and atomic hydrogen [Figs. 1(c) and S1(b)]. There are two different H_2 units within the structure of $P\bar{1}\text{-HfH}_{10.5}$,

and their H-H bond lengths are equal to 0.833 and 0.843 Å at 300 GPa, respectively, which are somewhat shorter than the $P6_3/mmc$ -HfH₁₀ (0.923–1.082 Å) and comparable to the $P\bar{1}$ -HfH₁₀ (0.811 and 0.939 Å) [39]. The monoclinic $C2/m$ -HfH₁₄ phase possesses H₂ units and atomic hydrogen in its structure, similar to the $P\bar{1}$ -HfH_{10.5} [Fig. 1(d)]. The sample was finally compressed isothermally to 302 GPa and there is no evidence of pressure-induced phase transition—the diffraction peaks only shift to the high 2θ angle region (smaller d -spacing) with raising the pressure [Fig. 1(a)]. In addition, cell No. 2 was prepared with Hf and AB loaded and compressed to 258 GPa at RT and laser heated at ~ 2200 K. The analysis of x-ray data reveals the mixed phase of $P\bar{1}$ -HfH_{10.5} and $C2/m$ -HfH₁₄, which behaves similarly to the case of cell No. 1 (Fig. S2 [58]).

With the purpose of collecting synchrotron x-ray diffraction and electrical resistivity data simultaneously, we loaded a ~ 2.0 - μm -thick Hf polycrystalline sample surrounded by excess of hydrogen together with four electrodes in a 20 μm diameter culet DAC (cell No. 3). After the hydrogen was loaded, the pressure was increased directly to 216 GPa at RT and the cell was kept at RT for one month to allow the chemical reaction of Hf and H₂. We found there are no obvious morphology changes in the sample [see Fig. 2(b)]. The synchrotron x-ray diffraction data reveal the formation of pure low stoichiometric hydride $Pm\bar{3}n$ -HfH₃ ($a = 3.1725(4)$ Å). In the cubic structure of $Pm\bar{3}n$ -HfH₃, the Hf atoms occupy the positions of vertex and center (like the bcc β -phase of Hf metal) and six faces are occupied by 12 H atoms. Thereafter, the sample was laser heated at ~ 2200 K, the appearance of diffraction images changed substantially, and pressure increased slightly to 220 GPa. The diffraction peaks were identified as mixed phases of $P\bar{1}$ -HfH_{10.5} and $C2/m$ -HfH₁₄ [Fig. 2(a)]. Moreover, we found the removal of $C2/m$ -HfH₁₄ is extremely difficult, and the shape of the opaque sample did not change substantially even when excess hydrogen surrounded the sample and cycles of laser heating were conducted (see Raman measurements after laser heating in Fig. S3 [60]). Like cell No. 1, there was no indication of phase transition after the pressure was increased to 235 GPa [Fig. 2(a)]. Further compression broke the diamonds, which may be caused by hydrogen penetrating the diamond body. We also loaded Hf metals together with AB in a DAC (cell No. 4) and compressed the sample to 220 GPa at RT. Before laser heating, synchrotron x-ray data at 220 GPa reveal the Hf metal in the bcc β -phase region [$a = 2.8462(6)$ Å], consistent with the equation of states of Hf from the previous reports [61,62]. After laser heated at ~ 2200 K, new diffraction peaks of $Pm\bar{3}n$ -HfH₃ and $Fddd$ -HfH₄ are indexed except for the unreacted Hf metal (Fig. S4 [58]). The appearance of the low stoichiometric hydrides is most likely due to the deficiency of hydrogen as provided by AB. The amount of AB is difficult to control before sample loading, especially at pressures above 200 GPa. X-ray data of the other two cells (cells No. 5 and 6) demonstrated that the cubic $Pm\bar{3}n$ -HfH₃ is the dominant phase [Fig. 3(c)].

From the refined experimental x-ray data, we plotted the lattice parameters of $P\bar{1}$ -HfH_{10.5} and $C2/m$ -HfH₁₄ phases as a function of pressure. As shown in Fig. 3(a), the experimental lattice parameters of $P\bar{1}$ -HfH_{10.5} are consistent with

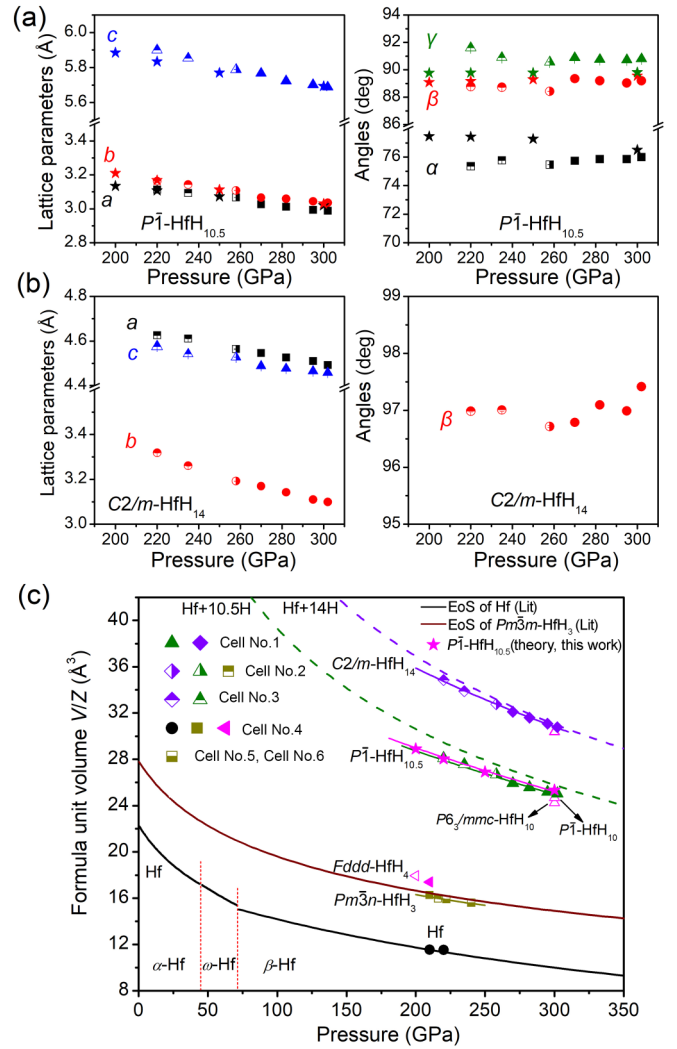


FIG. 3. (a), (b) Lattice parameters of $P\bar{1}$ -HfH_{10.5} and $C2/m$ -HfH₁₄ as a function of pressure. Data from different cells are indicated as half-filled and full symbols. (c) Formula unit of volume of the synthesized Hf-H compounds as a function of pressure. The $V(P)$ data of three phases of hafnium metal are from references. The transition pressures of α -Hf $\rightarrow$ ω -Hf $\rightarrow$ β -Hf are indicated as red dotted lines. The corresponding ideal mixing curves of Hf + 7H₂ (14H) and Hf + 5.25H₂ (10.5H) are plotted in dashed lines. Calculated equations of states are plotted in relative hafnium hydrides. The theoretical results of $P\bar{1}$ -HfH_{10.5} are represented as star symbols in all the panels.

the theoretical predictions (Table S4 [58]). The lattice parameter b reduced by $\sim 4.05\%$, whereas a and c decreased by 3.98% and 3.57%, respectively, which altogether yields the unit-cell volume reduction of 10.87% in the range of 220 to 302 GPa. The pressure stability range of the $P\bar{1}$ -HfH_{10.5} permitted it to calculate the $V(P)$ data of $P\bar{1}$ -HfH_{10.5} from the reaction products of cells No. 1–3 using the third-order Birch-Murnaghan EoS yielding $K_{170} = 33016$ GPa and its pressure derivative $K'_{170} = 2.7(1)$, which agrees well with the theoretical predictions ($K_{170} = 34718$ GPa and $K'_{170} = 2.6(1)$). In phase $C2/m$ -HfH₁₄, the b axis displayed the largest compressibility (reduced by $\sim 6.61\%$), while a and c axes shortened by 2.88% and 2.56%, respectively. The experimental $V(P)$

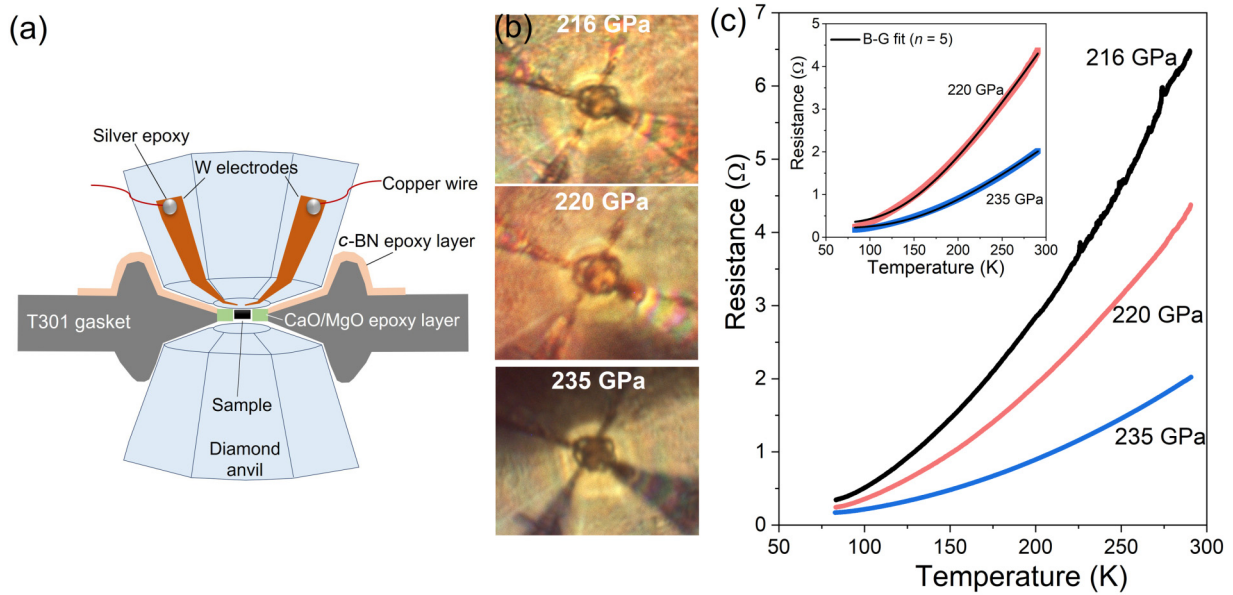


FIG. 4. (a) Scheme of the typical arrangement for the high pressure electrical resistance measurement in a DAC. (b) Images of the sample at different pressures of cell No. 3 with four electrodes before and after laser heating under reflection and transmission lights. (c) Temperature dependent electrical resistance as a function of temperature. The inset displays the standard B-G formula fit ($n = 5$) of $R(T)$ data at 220 and 235 GPa, respectively.

data of $C2/m\text{-HfH}_{14}$ can be fitted well with the third Birch-Murnaghan EoS with $V_0 = 119.95(15) \text{ \AA}^3$ and a bulk modulus $K_0 = 1955 \text{ GPa}$ as well as a pressure derivative of $K'_0 = 3.1(1)$. In addition, the second-order Birch-Murnaghan EoS fits to the $V(P)$ data of $Pm\bar{3}n\text{-HfH}_3$, yielding $K_0 = 1352 \text{ GPa}$ and $K'_0 = 4$, which is comparable to the theoretical predictions [145(2) GPa] [39].

Electrical resistance measurements were performed on cell No. 3 using the van der Pauw technique to study the possible existence of the high T_c superconductivity at megabar pressures. After keeping the loaded hafnium and hydrogen for one month at RT, we measured the electrical resistance of cell No. 3 at 216 GPa in the range of 80–290 K. The electrical resistance of synthesized $Pm\bar{3}n\text{-HfH}_3$ decreases gradually upon cooling, indicative of a typical metallic character. Such feature also can be clearly observed from the shiny luster appearance of the sample from the reflection light [Fig. 4(a)]. Then the sample was heated by a pulsed laser at $\sim 2200 \text{ K}$ (pressure slightly increased from 216 GPa to 220 GPa after heating), the electrical resistance of the formed product dropped about 1.5 times at 290 K but still no superconductivity was observed down to 80 K. After pressure was increased to 235 GPa, the room temperature x-ray data were collected before and after laser heating (performed at $\sim 2200 \text{ K}$), and we did not observe distinct diffraction pattern changes even when cycles of heating were conducted. Then cell No. 3 was cooled again in the cryostat, resulting in electrical resistance dropped by a factor of 2 at 290 K, while the $R(T)$ curve decreased with decreasing temperature. The temperature-dependent resistance $R(T)$ data of the synthesized superhydrides measured at 220 and 235 GPa were analyzed using the Bloch-Grüneisen (B-G) expression as a phenomenological description of the normal-state transport within the experimentally accessible temperature

range of 80–290 K [63,64],

$$R(T) = R_0 + B \left(\frac{T}{\Theta_D} \right)^n \int_0^{\Theta_D/T} \frac{x^n}{(e^x - 1)(1 - e^{-x})} dx,$$

where R_0 is the residual resistance of the sample, B is a fitting parameter, and Θ_D is the Debye temperature. In general, superconductivity in many superhydrides is commonly discussed within an electron-phonon pairing mechanism, as exemplified by H_3S [6,65]. However, because our resistivity measurements do not extend to lower temperatures, the present data do not allow a reliable determination of the microscopic scattering mechanism. Therefore, the $R(T)$ curves are discussed here only phenomenologically, and no claim is made regarding a specific transport mechanism or Fermi-liquid behavior. Using the standard B-G form with $n = 5$ fixed, the fits yield Debye temperatures of $\Theta_D = 1014.2 \text{ K}$ at 220 GPa and $\Theta_D = 1081.0 \text{ K}$ at 235 GPa, respectively [Fig. 4(c)]. The fitted Debye temperature shows a slight increase with pressure, which may be consistent with lattice hardening under compression; however, this trend should be interpreted cautiously because the values are effective fitting parameters rather than definitive thermodynamic quantities. In addition, the mixed phase nature of the sample, containing coexisting $P\bar{1}\text{-HfH}_{10.5}$ and $C2/m\text{-HfH}_{14}$ phases (Fig. 2), may further broaden the transport response and limit the quality of the fit. The measured $R(T)$ curves can be described qualitatively within the available temperature window, but a more definitive transport analysis would require additional low temperature measurements below 80 K. Accordingly, no superconducting transition is observed within the measured range down to 80 K, indicating that superconductivity, if present, emerges below the accessible temperature range. This feature implies that the synthesized compound including

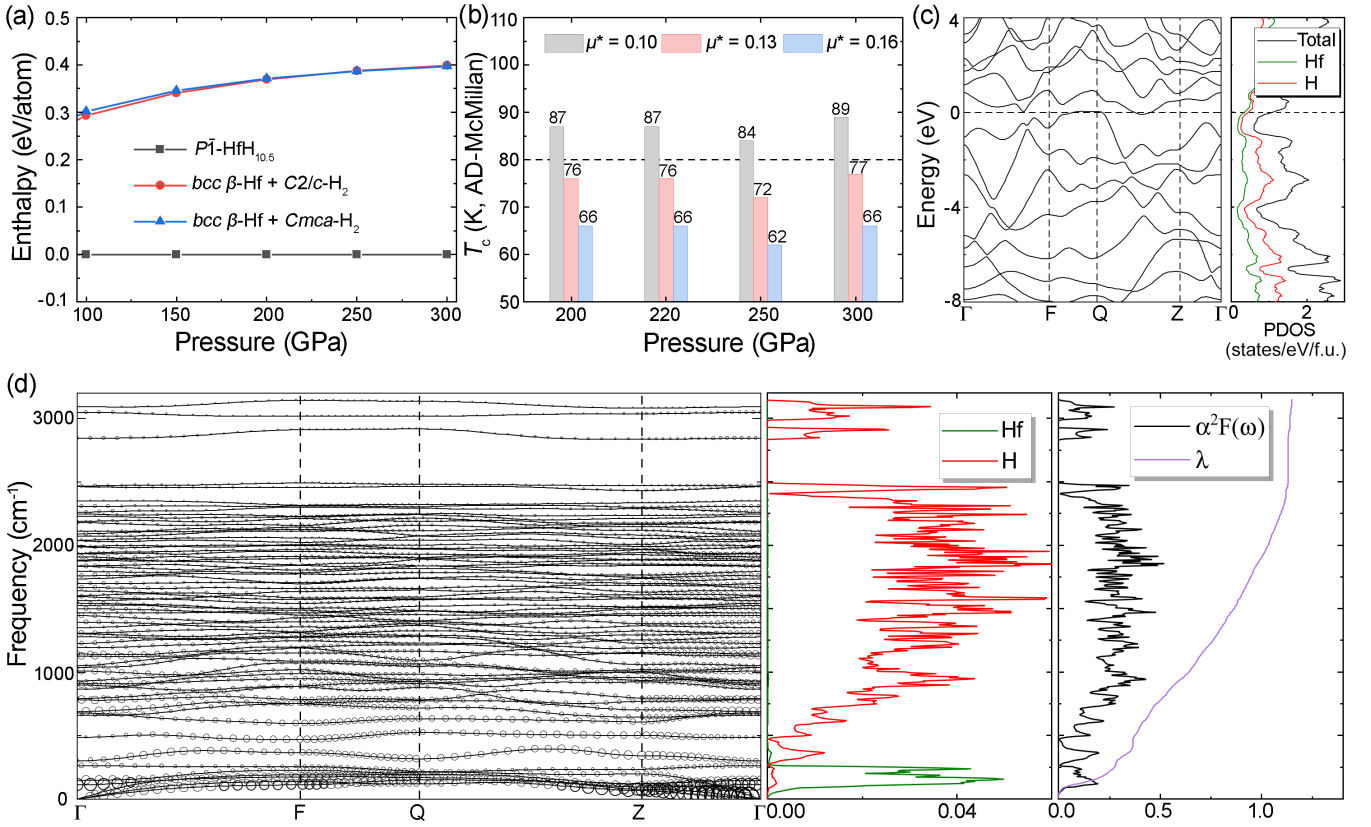


FIG. 5. (a) Formations of enthalpies of $P\bar{1}$ -HfH_{10.5} phase from $bcc\beta$ -Hf and C2/c-H₂ or Cmca-H₂. (b) Calculated superconducting temperatures of $P\bar{1}$ -HfH_{10.5} at different pressures (see Table S3). (c) Electronic band structure (left panel) and projected density of states (right panel) of $P\bar{1}$ -HfH_{10.5} at 300 GPa. (d) Phonon dispersion curves with the strength of q -resolved λ_q indicated by circle size, projected phonon densities of states (PHDOS), and isotropic Eliashberg spectral function $\alpha^2F(\omega)$ as well as EPC parameter $\lambda(\omega)$ of $P\bar{1}$ -HfH_{10.5} at 300 GPa.

$P\bar{1}$ -HfH_{10.5} and C2/m-HfH₁₄ phases is not a high T_c superconductor, consistent with the estimated low- T_c values of 62–89 K in $P\bar{1}$ -HfH_{10.5} at 200–300 GPa [as shown in Fig. 5(b)] and superconductivity of C2/m-HfH₁₄ (reported by Zhang *et al.* in Ref. [44]).

Further simulations of the electronic properties [Fig. 5(c)] and electron-phonon coupling properties [Fig. 5(d)] of $P\bar{1}$ -HfH_{10.5} at 300 GPa reveal this phase is dynamically stable, but it does not show high temperature superconductivity due to the existence of H₂ molecules within its structure. A major proportion of hydrogen electrons in H₂ molecules inevitably occupy the low-energy molecular bonding orbitals far below Fermi level, while only a small proportion of hydrogen electrons occupy the high-energy molecular nonbonding orbitals near the Fermi level. As a result, though 28% of H atoms [6 in 21 H atoms, as shown in Fig. 1(c)] in $P\bar{1}$ -HfH_{10.5} form H₂ molecules, only very few H electrons in H₂ contribute to the electron density of state at the Fermi level N_{Ef} , and thus H₂ molecules contribute only 1.6% (2800–3200 cm⁻¹) of the total electron-phonon coupling parameter λ . On the other hand, atomic-H contributed mainly (300–2500 cm⁻¹) to the λ , which inspired us with an idea that higher- T_c might be expected with all H₂ dissociated into atomic H. The dissociation of H₂ molecules usually requires higher pressure or introduction of additional electrons, which might be an interesting topic for future research.

IV. CONCLUSIONS

In summary, we successfully synthesized hafnium superhydride $P\bar{1}$ -HfH_{10.5} together with other previously predicted phases, including $Pm\bar{3}n$ -HfH₃, $Fddd$ -HfH₄, and C2/m-HfH₁₄, through the chemical reaction of hafnium and hydrogen or AB in laser-heated diamond anvil cells. The recent predicted high temperature superconductor $P6_3/mmc$ -HfH₁₀ with high T_c above 210 K at 250 GPa was not observed in our experiments in the range of 200 to 302 GPa. The $P\bar{1}$ -HfH_{10.5} phase consisted of atomic hydrogen and H₂ molecular units in its crystal structure, which is most likely responsible for the absence of superconductivity down to ~80 K in the electrical resistance measurements. Theoretical calculations revealed that $P\bar{1}$ -HfH_{10.5} stabilizes in the range of 170–300 GPa and its estimated critical temperature is typically lower than 80 K, consistent with the experimental data. Our results provide solid evidence that the emergence of H₂-like units within the crystal structures of superhydrides contribute to the low superconducting temperature.

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DATA AVAILABILITY

There are no publicly available research data or software supporting this manuscript. Requests for further information or data should be sent to the authors.

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