Flourishing rare earth superhydrides are a class of recently discovered materials that exhibit near-room-temperature superconductivity at high pressures, ushering in a new era of superconductivity research at high pressures. Yttrium superhydrides drew the most attention among these superhydrides due to their abundance of stoichiometries and excellent superconductivities. Here, we carried out a comprehensive study of yttrium superhydrides in a wide pressure range of 140 GPa–300 GPa. We successfully synthesized a series of superhydrides with the compositions of YH$_6$, YH$_8$, YH$_7$, and YH$_9$, and reported superconducting transition temperatures of 82 K at 167 GPa, 218 K at 165 GPa, 29 K at 162 GPa, and 230 K at 300 GPa, respectively, as evidenced by sharp drops in resistance. The structure and superconductivity of YH$_4$ were taken as a representative example and were also examined using x-ray diffraction measurements and the superconductivity suppression under external magnetic fields, respectively. Clathrate YH$_{10}$, a candidate for room-temperature superconductor, was not synthesized within the study pressure and temperature ranges of up to 300 GPa and 2000 K. The current study established a detailed foundation for future research into room-temperature superconductors in polynary yttrium-based superhydrides.

Keywords: high pressure, superhydride, superconductivity

PACS: 62.50.–p, 74.70.–b, 05.70.Fh, 74.62.Bf

DOI: 10.1088/1674-1056/ac872e

1. Introduction

The search for high-temperature superconductors (HTS) with superconducting transition temperature ($T_c$) above liquid-nitrogen temperature has long been recognized as an intriguing topic since the discovery of Hg with $T_c = 4.2$ K. According to the Bardeen–Cooper–Schrieffer theory, metallic hydrogen (MH) is one of the best candidates for achieving HTS; however, the quest for MH has proven extremely challenging due to the requirements of ultrahigh pressure conditions. Satterthwaite et al. discovered $\sim 8$ K superconductivity in thorium hydride in 1970, implying that hydrogen-rich metal hydrides would be HTS. Then, Gilman and Ashcroft further proposed that MH could be achieved in hydrogen-rich compounds at lower pressures because the heavier atoms played a chemical precompression role in hydrogen, ushering in a new era of HTS research in hydrogen-rich compounds at high pressures. However, despite significant efforts, there were no experimental breakthroughs for a long time until the observation of 203 K superconductivity at 155 GPa in covalent H$_3$S, which further inspired the search for HTS in conventional phonon-mediated hydride superconductors.

In contrast to covalent superhydrides such as H$_3$S, ionic metal hydrides offer more options for finding HTS. Wang et al. (2012) predicted the first CaH$_6$ clathrate hydride with a very high $T_c$ of 235 K at 150 GPa. Following this study, a long list of clathrate REH$_6$ (RE: rare earth metal) were predicted to have high $T_c$ values close to or even above room temperature. Stimulated by these predictions, a series of clathrate superhydrides, such as CaH$_6$,$^{11}$ LaH$_{10}$,$^{12,13}$ CeH$_8$, CeH$_{10}$,$^{14}$ ThH$_9$, ThH$_{10}$,$^{15}$ (La, Y)H$_{10}$,$^{16}$ were successfully synthesized with $T_c$ ranging from 57 K–260 K. Among ionic superhydrides, yttrium superhydrides piqued the interest of researchers due to their abundant stoichiometries, they are predicted to have high $T_c$ values close to or even above room temperature. Furthermore, Troyan et al. also independently synthesized a clathrate YH$_6$, with an observed $T_c$ of 224 K at 166 GPa. Following that, Snider et al. synthesized YH$_6$ with a $T_c$ of up to 262 K using catalytic hydrogenation at about 182 GPa. Furthermore, recent research has successfully observed 88 K superconductivity of...
Besides binary yttrium superhydrides, yttrium-bearing ternary hydrides, where the introduction of a third element other than hydrogen considerably expands the phase space, have attracted extensive attention. Liang et al.\textsuperscript{[22]} and Xie et al.\textsuperscript{[23]} predicted a clathrate CaYH\textsubscript{12} with an estimated \(T_c\) of 258 K at 200 GPa and 230 K at 180 GPa, respectively. Then, Liang et al. predicted a ternary YSH\textsubscript{6} with a \(T_c\) of 91 K at 210 GPa\textsuperscript{[24]} (La, Y)H\textsubscript{6} and (La, Y)H\textsubscript{10}\textsuperscript{[16]} were synthesized experimentally at high pressures with \(T_c\)s of 237 K and 253 K, respectively.

Previous research has primarily concentrated on HTS (\(T_c > 200\) K), even though more superhydrides have been synthesized. Thus far, there has been a dearth of efforts to systematically investigate the superconductivity of all experimentally reported unconventional superhydrides. In this work, we first conducted detailed structure and superconductivity studies of YH\textsubscript{4}, which was chosen as an example due to its rare previous investigation. X-ray diffraction measurements revealed the successful synthesis of predicted \(I4/mmm\)-YH\textsubscript{4} at about 167 GPa and 1600 K, and its measured \(T_c\) of 82 K was evidenced by a sharp drop in resistance and a characteristic decrease in superconducting transition under a magnetic field up to 8.5 T. Further electrical transport measurements revealed a series of additional superconducting transitions at 29 K (162 GPa), 218 K (165 GPa), and 230 K (300 GPa), which arise from YH\textsubscript{7} and clathrate structured YH\textsubscript{6} and YH\textsubscript{9}, respectively, inferred from \(T_c\)s consistency with previous studies.

2. Experimental methods

According to the different target pressures, symmetric diamond anvil cells (DACs) outfitted diamond anvils with a cubit size of \(\sim 30\) \(\mu\text{m}\)–60 \(\mu\text{m}\) beveled at 8.5\textdegree{} to a diameter of \(\sim 250\) \(\mu\text{m}\). The composite gasket was composed of rhenum outer annulus and a mixture of epoxy resin and Al\textsubscript{2}O\textsubscript{3} powder. The insulating gasket was pre-indentet to a thickness of 10 \(\mu\text{m}\), and the corresponding sample chamber with a diameter of 20 \(\mu\text{m}\)–30 \(\mu\text{m}\) was drilled using a laser drilling system. Commercially available yttrium ingot (Alfa Aesar, 99.9\% purity) and NH\textsubscript{3}BH\textsubscript{3} (AB) powder (Sigma-Aldrich, 97\%) were loaded into the sample chamber inside a glovebox filled with Ar atmosphere with O\textsubscript{2} and H\textsubscript{2}O contents of \(< 0.01\) ppm. The Y foil and Au electrodes with thicknesses of 2 \(\mu\text{m}\) and 1 \(\mu\text{m}\), respectively, were sandwiched between the AB layers. The application of Au electrodes can effectively avoid the chemical reaction\textsuperscript{[25]} between the electrodes and hydrogen, which can result in the formation of undesirable superconductors, as well as help to maintain a hydrogen-rich environment. AB serves as a hydrogen source while also acting as thermal insulation layers. Subsequently, the samples were compressed to the required synthesis pressure. The pressure in the sample chamber was calibrated using the high-frequency edge of the diamond Raman line.\textsuperscript{[26]} The laser heating of the sample was performed using a pulsed YAG infrared laser, and the temperature was determined using the black-body radiation fit within the Planck function. \textit{In situ} high-pressure angle-dispersive x-ray diffraction (ADXRD) experiments were performed at the Shanghai Synchrotron Radiation Facility’s BL15U1 beamline (5 \(\mu\text{m}\) × 12 \(\mu\text{m}\)) with a monochromatic beam wavelength of 0.6199 \(\AA\) and an average acquisition time of 120 s. Before the experiment, the relevant geometric parameters were calibrated using a CeO\textsubscript{2} standard. Diffraction patterns were collected using a Mar165 CCD detector and analyzed using DIOPTAS software, yielding one-dimension profiles.\textsuperscript{[27]} The Le Bail profile matching refinements were performed using the GSAS + EXPGUI programs.\textsuperscript{[28]} Based on the four-probe van der Pauw method\textsuperscript{[29]} the resistance measurements were performed with currents of \(10^{-6}–10^{-4}\) A (Keithley 2182A nanovoltmeter and 6221 AC and DC source) and the selected data were warming cycles with a controlled rate of approximately 1 K min\textsuperscript{-1}. Furthermore, non-magnetic DACs made of Be-Cu alloy were used for resistance measurements in an external magnetic field of up to 8.5 T.

3. Results and discussion

In this work, we prepared 11 samples, labeled as samples 1 through sample 11, to synthesize yttrium superhydrides from a mixture of Y and AB, and explore their superconductivity. Previous excellent results have shown AB to be a reliable H\textsubscript{2} source.\textsuperscript{[11,13,18,19,21]} At high temperatures, AB would decompose into H\textsubscript{2} plus c-BN, the latter avoiding the problem of poor contact between the synthesized product and electrodes. The diagram of the assembly used for synthesis and four-probe electrical resistance measurements is shown in Fig. 1(a). In sample 1, the reactants were compressed to 167 GPa [Fig. S1(a)] before being heated to about 1600 K. The clear H–H vibration from H\textsubscript{2} molecular [Fig. S1(b)] demonstrates a hydrogen-rich environment. The sample turned black after laser heating, indicating that a chemical reaction occurred [inset in Fig. 1(b)]. Representative electrical resistance measurements as a function of temperature reveal a superconducting transition at 82 K, as evidenced by the sharp drop in the resistance, as shown in Fig. 1(b). This superconducting transition can be perfectly reproduced in several independent experiments (Fig. 2 and Fig. S2), further confirming the reliability of our results. To determine the highest value of \(T_c\), we evaluated the pressure dependence of \(T_c\), as shown in Fig. 2(b). \(T_c\) fluctuates in the pressure range of 145 GPa–170 GPa in different experiments and the highest \(T_c\) of 84 K at 162 GPa is consistent with the previous theoretical estimate of 84 K–95 K for YH\textsubscript{4}. Furthermore, as pressure decreases, the superconducting transition disappears at about 143 GPa [Figs. S2(a) and S2(b)], indicating a possible superconducting phase decomposition.
Fig. 1. (a) Schematic of the experimental setup for synthesis and four-probe superconducting electrical resistance measurements. (b) Temperature dependence of resistance in sample 1 (S1) at 167 GPa. The insets show an optical micrograph of the sample before and after laser heating. The value of the \(T_c\) is defined as the crossing point of the resistance slopes before and after the resistance drop. (c) Synchrotron XRD pattern of S1 at 167 GPa. The inset displays a two-dimensional XRD pattern. Unidentified weak reflections are marked by asterisks. (d) Crystal structures of \(I_{4/mmm}\)-YH\(_3\) and \(I_{4/mmm}\)-YH\(_4\). Big and small balls represent Y and H atoms, respectively.

Fig. 2. (a) Temperature dependence of resistance in sample 3 (S3) at 162 GPa. Inset: crystal structures of \(Imm2\)-YH\(_7\). Big and small balls represent Y and H atoms, respectively. (b) Pressure dependence of \(T_c\) for \(I_{4/mmm}\)-YH\(_4\) (circle) and \(Imm2\)-YH\(_7\) (star). Different colors represent different samples. The cited experimental data for YH\(_4\) are represented by open circles. Dark cyan symbols depict the calculated data from Troyan et al.\(^{[18]}\)
To further determine the structure of the high-temperature superconducting phase, we performed in situ high-pressure ADXRD measurements of sample 1, which revealed that the products were dominated by $I4/\text{mmm}$-$\text{YH}_3$ and $I4/\text{mmm}$-$\text{YH}_4$ as shown in Fig. 1(c) and the refined structural information is listed in Table S1. The tetragonal $\text{YH}_3$, which possessed a new high-pressure phase in addition to the conventional fcc phase, was synthesized for the first time after prediction. Moreover, no superconductivity was predicted in $I4/\text{mmm}$-$\text{YH}_3$ up to 200 GPa. Consequently, the observed-superconducting transition in sample 1 should be attributed to $\text{YH}_4$.

Due to the small sample size, measuring the Meissner effect in ultra-high-pressure experiments remains a significant challenge to this day. An applied external magnetic field can break the Cooper pairs, reducing the value of $T_c$; thus, the suppression of superconducting transitions by an applied magnetic field can be used to investigate the nature of the superconducting states. Figure 3(a) shows the measured resistance of sample 2 under different magnetic fields at 170 GPa. The $T_c$ decreased from 77 K to 53 K as the magnetic field increased to 8.5 T, indicating the superconducting nature of the transition. The extrapolated upper critical field $\mu_0H_{c2}(T)$ and coherence length toward $T = 0$ K are 14.9 T and 47 Å, as well as 18.7 T and 42 Å, respectively, as shown in Fig. 3(b), and were fitted by the Ginzburg–Landau (GL) and Werthamer–Helfand–Hohenberg (WHH) models.[31] Furthermore, besides the superconductivity of $\text{YH}_4$, we observed another low-temperature superconductivity of 17 K [inset in Fig. 3(a)] in this experiment, which can be attributed to the element yttrium based on the agreement with the $T_c$ of the unheated sample (Fig. S3). Similar results for $\text{YH}_4$ were independently reported by another group.[21]

Furthermore, after laser heating sample 3 to approximately 1750 K at 162 GPa, we observed step-down behavior in electrical resistance measurements at 81 K, 29 K, and 18 K (Fig. 2(a)). As aforementioned, the first and third resistance drops, result from superconducting transitions of $\text{YH}_4$ and element Y, respectively. Based on previous theoretical work,[18] we hypothesized that the second resistance drop at 29 K may originate from the superconducting transition of $\text{Imm}_2$-$\text{YH}_7$, which was also reproduced in sample 7 [Fig. S2(c)]. Figure 2(b) summarizes the pressure dependency of $T_c$ for $\text{YH}_7$ and $\text{YH}_4$. Similar to the variation trend of $\text{YH}_4$, the $T_c$ of $\text{YH}_7$ was relatively stable in the pressure range of 142 GPa–170 GPa. Although both $I4/\text{mmm}$-$\text{YH}_4$ and $\text{Imm}_2$-$\text{YH}_7$ have a molecular “H$_2$” unit [Fig. 1(d) and Fig. 2(a)], the $T_c$ of $\text{YH}_4$ with a high-symmetry structure is higher than that of $\text{YH}_7$ due to stronger electron-phonon coupling.[18]

In the following work, we tuned the heating temperature and pressure, to synthesize the high-temperature superconducting clathrate $\text{YH}_6$, $\text{YH}_9$, or even $\text{YH}_{10}$. When we increased the heating temperature to 2200 K at 165 GPa for sample 4, a $T_c$ of 218 K was observed, as shown in Fig. 4(a). Subsequently, sample 5 was compressed to a superhigh pressure of 300 GPa [Fig. S1(a)] and heated to about 2000 K, and the electrical resistance measurement curve revealed superconductivity at 230 K (Fig. 4(a)). As shown in Fig. 4(b) the $T_c$s of samples 4 and samples 5 perfectly match the reported experimental results for clathrate structured $\text{YH}_6$ and $\text{YH}_{9}$.[18,19] The high $T_c$ of $\text{Imm}_3$-$\text{YH}_6$ and $P6_3/mmc$-$\text{YH}_9$ was attributed to their hydrogen cage structure, and particularly the significant contribution of the H-derived electronic density of states at the Fermi level.[8,10] Unfortunately, we found no evidence of clathrate $\text{YH}_{10}$, which may be synthesized at higher pressures.
A series of superhydrides with high $T_c$ have been synthesized under high pressures; however, the absence of resistive transition broadening with increasing magnetic field in some works\cite{12,16,32} has led to a debate about their superconductivity.\cite{33} Using YH$_4$ as an example, we observed a clear broadening of the resistive transition under applied magnetic fields (Fig. S4), which follows a similar trend to that of typical standard superconductors such as MgB$_2$\cite{34} and NbN,\cite{35} further demonstrating the veracity of our results. As a member of superhydride, the results of electrical transport measurements under external magnetic fields in YH$_4$ will help clarify the debate on the superconductivity in superhydrides.

4. Conclusion and perspectives

In summary, we have successfully synthesized YH$_4$, YH$_6$, YH$_7$, and YH$_9$, which exhibited $T_c$'s of 82 K at 167 GPa, 218 K at 165 GPa, 29 K at 162 GPa, and 230 K at 300 GPa, respectively. Furthermore, a tetragonal phase as a new high-pressure structure of conventional YH$_3$ was synthesized for the first time at 167 GPa. These findings confirm the original theoretical prediction and provide a foundation for future research into HTS on the doped Y-based polynary superhydrides.

Acknowledgments

XRD measurements were performed at BL15U1 station in Shanghai Synchrotron Radiation Facility (SSRF) and 4W2 station in Beijing Synchrotron Radiation Facility (BSRF). The measurements of superconducting transition under external magnetic fields were supported by the Synergic Extreme Condition User Facility (SECUF) and China’s Steady High Magnetic Field Facility (SHMFF).

Project supported by the National Key Research and Development Program of China (Grant Nos. 2021YFA1400203 and 2018YFA0305900), the National Natural Science Foundation of China (Grant Nos. 52090024, 11874175, 12074139, 12074138, 11874176, and 12034009), the Strategic Priority Research Program of Chinese Academy of Sciences (Grant No. XDB33000000), and Program for JLU Science and Technology Innovative Research Team (JLUSTIRT).

References

[1] Onnes H K 1911 Commun. Phys. Lab. Univ. Leiden, b 120
[2] Bardeen J, Cooper L N and Schrieffer J R 1957 Phys. Rev. 108 1175
[3] Satterthwaite C B and Toepke I L 1970 Phys. Rev. Lett. 25 741
[4] Gilman J J 1971 Phys. Rev. Lett. 26 546
[5] Ashcroft N W 2004 Phys. Rev. Lett. 92 187002
[6] Drozdov A P, Eremets M I, Troyan I A, Ksenofontov V and Shylin S I 2015 Nature 525 73
[7] Wang H, Tse J S, Tanaka K, Iitaka T and Ma Y M 2012 Proc. Natl. Acad. Sci. USA 109 6463
[8] Peng F, Sun Y, Pickard C J, Needs R J, Wu Q and Ma Y M 2017 Phys. Rev. Lett. 119 107001
[9] Liu H Y, Naumov I I, Hoffmann R, Ashcroft N W and Hemley R J 2013 Proc. Natl. Acad. Sci. USA 114 6990
[10] Li Y W, Hao J, Liu H Y, Tse J S, Wang Y C and Ma Y M 2015 Sci. Rep. 5 9948
[11] Ma L, Wang K, Xie Y, Yang X, Wang Y Y, Zhou M, Liu H Y, Wang H B, Liu G T and Ma Y M 2022 Phys. Rev. Lett. 128 167001
[12] Drozdov A P, Kong P P, Minkov V S, Bresdin S P, Kuzovnikov M A, Mozzafari S, Balicas L, Balakirev F F, Graf D E, Prakapenka V B, Greenberg E, Knyazev D A, Tkacz M and Eremets M I 2019 Nature 569 528
[13] Sonnayazulu M, Ahart M, Mishra A K, Geballe Z M, Baldini M, Meng Y, Struzhkin V V and Hemley R J 2019 Phys. Rev. Lett. 122 027001

Fig. 4. (a) Temperature dependence of resistance in sample 4 (S4) at 165 GPa and sample 5 (S5) at 300 GPa. The large residual resistance in S4 and S5 is mainly from the coexistence of multiple phases. Furthermore, the pseudo-four-electrode method was used in the electrical measurement for S5, thus introducing additional resistance from the electrodes. Inset: crystal structures of Im3m-YH$_6$ and P6$_3$/mmc-YH$_6$. Big and small balls represent Y and H atoms, respectively. (b) Pressure dependence of $T_c$ for Im3m-YH$_6$ (star) and P6$_3$/mmc-YH$_6$ (hexagon). The symbols of dark cyan, orange, and red correspond to the data of Kong et al.\cite{19} Troyan et al.,\cite{34} and this work, respectively.
