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Possible superconductivity at ~70 K in tin hydride SnH_x under high pressure

F. Hong [a, b, c, 1, **], P.F. Shan [a, b, 1], L.X. Yang [d, 1], B.B. Yue [d], P.T. Yang [a], Z.Y. Liu [a], J.P. Sun [a, b], J.H. Dai [a], H. Yu [a, b], Y.Y. Yin [a], X.H. Yu [a, b, c, ***], J.G. Cheng [a, b, *], Z.X. Zhao [a, b]

[a] Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China
[b] School of Physical Sciences, University of Chinese Academy of Sciences, Beijing, 100190, China
[c] Songshan Lake Materials Laboratory, Dongguan, Guangdong, 523808, China
[d] Center for High Pressure Science & Technology Advanced Research, Beijing, 100094, China

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ABSTRACT

Hydrides of air non-sensitive IVA-group elements were predicted to be possible high temperature superconductors (HTS) by N.W. Ashcroft (PRL **92**, 187002 (2004)), which inspired the exploration of hydrogen dominated metallic alloy-based HTS. Although the IVA-group hydrides have been investigated theoretically by several groups, the experimental realization of any superconducting IVA-group hydrides is still lacking. Here, we report on the observation of the possible superconducting transition at ~70 K in a SnH_x sample synthesized by laser heating Sn and ammonia borane inside a diamond anvil cell at ~200 GPa. The main phase of the obtained sample can be indexed with the monoclinic $C2/m$ SnH_{12} via comparison with the theoretical structural modes, which have distinct H-network with respect to the clathrate-type structure. A sudden drop of resistance and the systematic downward shift under external magnetic fields signal the occurrence of superconductivity in SnH_x with an upper critical field $\mu_0 H_{c2}(0) \approx 11.2$ T, and the resistive broadening behavior in magnetic fields follows the trend of traditional standard superconductors. This work provides an alternative way to obtain metal hydrides HTS via p electron-metals rather than the active s or f electron-metals (such as Mg, Ca, La, Y, Ce), which will stimulate the experimental exploration of hydrides HTS in different element groups.

1. Introduction

The hydrogen has been predicted to be a metal and even a high-temperature superconductor (HTS) under high pressure [1–3]. Much effort has been devoted to obtain the metallic hydrogen [3], but solid experimental evidence is still lacking to date [4]. To achieve a metallic state in hydrogen under attainable pressures, Ashcroft proposed a "pre-compression" mechanism in the hydrogen dominated metallic alloys, which could be promising HTS [5]. In this seminal work [5], Ashcroft stated that hydrides of IVA-group elements should be metallic and superconducting within the pressure capability of diamond anvil cell. Motivated by this idea, there are several theoretical investigations about the hydrides of IVA-group elements under high pressure. For CH_4, a series of phase transforms upon compression, from $I\text{-}43m$ to $Pmn2_1$ to $P2_1/c$ to $Pnma$, was found in calculations, and the $Pnma$ phase should be an insulator up to 150 GPa [6]. Experimentally, Raman measurements up to 288 GPa confirmed that CH_4 is still an insulator rather than a metal [7,8]. Other forms of carbon hydrides, such as $CH_4(H_2)_2$, $(CH_4)_2H_2$, $CH_4(H_2)_4$, can be synthesized under pressure [9], but whether they are metal or superconductor has not been examined. According to theoretical calculations, SiH_4 in the monoclinic structure could be a superconductor with $T_c = 45$–55 K at relatively low pressure (65–150 GPa) [10], and its T_c can research 106 K when increasing pressure to 610 GPa [11]. Superconducting

* Corresponding author. Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China.
** Corresponding author. Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China.
*** Corresponding author. Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China.
E-mail addresses: hongfang@iphy.ac.cn (F. Hong), yuxh@iphy.ac.cn (X.H. Yu), jgcheng@iphy.ac.cn (J.G. Cheng).
[1] F. Hong, P.F. Shan and L.X. Yang have equal contribution.

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SiH_8 could be energetically stable in the *Ccca* structure above 248 GPa with T_c of 98–107 K [12]. For GeH_4, it was reported to be metallized near 72 GPa [13] in the *I*4/*mmm* structure, while another group claimed that GeH_4 can form a *Cmmm* structure with superconducting transition near T_c = 54 K at 20 GPa [14]. GeH_8 was predicted to undergo several structural transitions and becomes superconductor above 220 GPa in the $P2_1/c$ structure with T_c = 76–90 K at 250 GPa [15]. Sn hydrides have been studied theoretically by several groups, and SnH_4, SnH_8 and SnH_{12} are all promising superconductors with T_c ranging from 15 to 97 K [16–18]. *C*2/*m*-PbH_8 can be stabilized above 133 GPa with a high T_c near 107 K at 230 GPa [19]. Although all these IVA-group hydrides, except for the carbon hydrides, could potentially be superconductors, experimental verifications are rather scarce so far. (Note: the reported superconducting behavior in SiH_4 at T_c ~ 17 K at 96 or 120 GPa in 2008 was later found to originate from the reacted Pt electrodes in form of PtH [20–23].)

Recently, several important breakthroughs have been achieved in fulfilling the goal of (near) room-temperature HTS by compressing the hydrogen-rich materials to megabar pressures [24–28]. Drozdov and Eremets et al. first discovered the superconductivity in H_3S with T_c = 203 K at ~ 155 GPa [24]. Then, lanthanum superhydride LaH_{10} was reported with T_c = ~ 250–260 K at 170–190 GPa [25,26,29]. Subsequently, several other rare-earth superhydrides with similar clathrate structures have been synthesized [30–35] and high-T_c superconductivity was discovered, *e.g.* in YH_9 (T_c = 243 K at 201 GPa) [36] and ThH_{10} (T_c = 161 K at 175 GPa) [27]. Snider et al. reported the observation of room-temperature superconductivity with the maximum T_c = 287 K at 267 GPa in a C–S–H system [28], and theoretical calculation shows that hole-doped (C or Si) H_3S could achieve such high T_c transition [37]. Among these works, except H_3S and C–S–H systems, which are covalent-like systems, all the other hydrides are formed by active metals with s or f electrons [27,30,31,33,36,38,39].

Despite of these progresses on hydrides, it is still a puzzle whether HTS can be achieved in the IVA-group hydrides, for which the IVA-group elements are located at the boundary between nonmetal and metal. To answer this question has a great implication, not just for the theoretical development and calculation methodology, but also for the experimental explorations of HTS. To this end, we tentatively synthesize the SnH_x experimentally. According to previous theoretical prediction, SnH_x could be stabilized in various forms, such as SnH_4, SnH_8, SnH_{12} [16–18]. For SnH_4, the *Ama*2 phase (Fig. 1(a)) is stable in the pressure range 96–180 GPa, above which it transforms to a hexagonal $P6_3/mmc$ phase (Fig. 1(b)) [16]. Both phases are predicted to be superconductors with T_c values of 15–22 K at 120 GPa and 52–62 K at 200 GPa for *Ama*2 and $P6_3/mmc$ phase, respectively [16]. By using evolutionary algorithm USPEX package, Esfahani et al. found that the hydrogen content in SnH_x could be much higher at pressure above 200 GPa [18]. The *I*4*m*2 SnH_8, *C*2/*m* SnH_{12} and SnH_{14} in Fig. 1(c and d) were found in calculations to be stable at pressures above 220, 250, and 280 GPa, respectively [18]. As shown in Fig. 1, the crystal structure symmetry of SnH_x is lowered with increasing pressure, and the H_3 and H_4 molecular units appear in the lattice. For these latter phases, the predicted T_c values are 81 K (SnH_8 at 220 GPa), 93 K (SnH_{12} at 250 GPa) and 97 K (SnH_{14} at 300 GPa), respectively [18]. Different from the clathrate hydrides, SnH_x represents another class of binary hydrides that can have much higher H content (*e.g.* MgH_{16} [40]) by incorporating a large amount of H_2, H_3, and/or H_4 molecular units in the lattice, the electronic density of sates near Fermi level have significant contributions from both Sn and H atoms, and the intermediate frequency H–H wagging and bending vibrations make a dominate contribution to the electron-phonon coupling [18]. In this

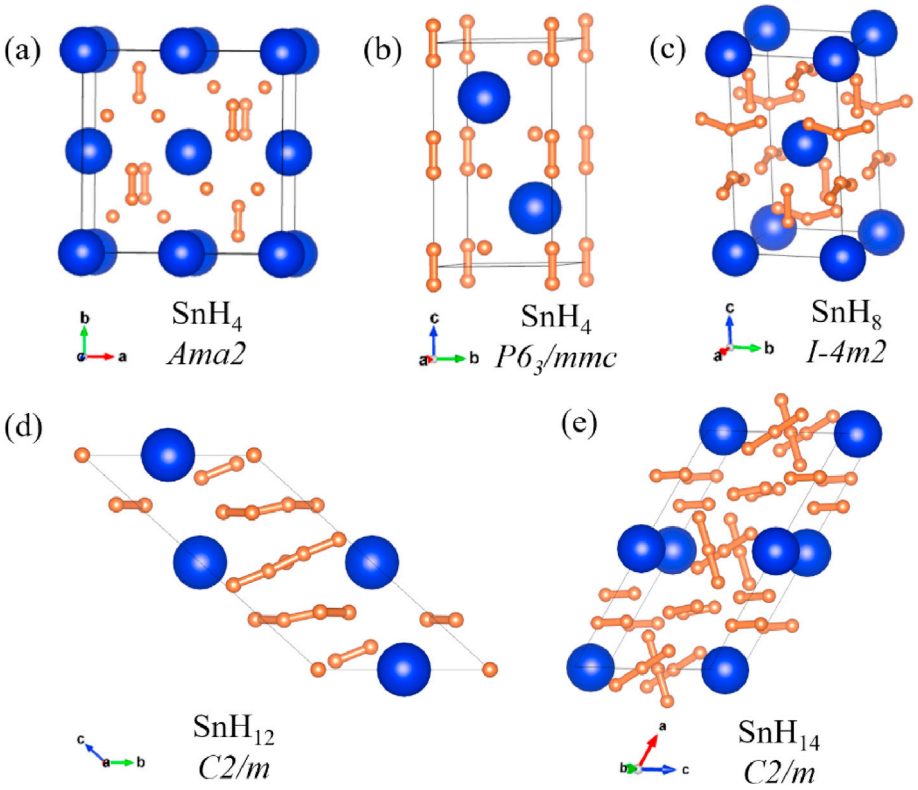

Fig. 1. (Color online) Theoretical structure models proposed for various SnH_x. (a) SnH_4 with space group *Ama*2 (96–180 GPa) [16], (b) SnH_4, $P6_3/mmc$ (> 180 GPa) [16], (c) SnH_8, *I*4*m*2 (> 220 GPa) [18], (d) SnH_{12}, *C*2/*m* (> 250 GPa) [18], (e) SnH_{14}, *C*2/*m* (> 280 GPa) [18].

work, we successfully observed the possible superconducting transition at ~70 K in a SnH_x sample at ~200 GPa and the XRD pattern of synthesized sample to some extent matches the simulated one based on the structural model of $C2/m$ SnH_{12} predicted recently.

2. Methods

For the in-situ synthesis and the subsequent four-probe resistance measurement of SnH_x, we followed the similar procedure developed in our recent work on LaH_{10} [29]. A thin Sn flake of 2 μm × 10 μm × 50 μm was loaded into a DAC (culet size of 50 μm) filled with ammonia borane (AB), we heated the central region of Sn + AB at ~200 GPa and ~1700 K by using a continuous 1064-nm YAG laser with 3–5 shots, each shot lasting <100 ms. As shown in Fig. 2(a and b), the sample after laser heating retains almost the initial configuration. The pressure values before and after laser heating were determined from the Raman signal of diamond [41,42]. We also calibrated the pressure by measuring the lattice constant of the Pt electrode near the sample by synchrotron XRD. From the Raman spectra of diamond, the pressure at the culet center was determined to be ~200 GPa and it remains nearly constant after laser heating. The pressure value is also well consistent with that marked by Pt, *i.e.* ~ 206 GPa. Synchrotron XRD at room temperature was performed at Shanghai Synchrotron Radiation Facility (SSRF, Beamline 15U) with a wavelength $\lambda = 0.6199$ Å and beam size of ~ 2 μm × 2 μm. The temperature-dependent resistance of the SnH_x sample after XRD measurements was measured in a sample-in-vapor ^{4}He cryostat equipped with a 9 T helium-free superconducting magnet.

3. Results and discussion

As illustrated in the top panel of Fig. 2 (c), the collected XRD patterns are a little bit spotty, which indicates that the crystal size of the SnH_x sample is on the scale of micron or submicron. As seen in the lower panel of Fig. 2(c), only five diffraction peaks can be well identified and there is a strong diffusing peak near 2θ ~ 18°. By comparing with the theoretically predicted structure models shown in Fig. 1, we find that the obtained SnH_x sample should be dominated by $C2/m$ SnH_{12} (simulated lattice parameters: $a = 5.179$ Å, $b = 3.038$ Å, $c = 7.364$ Å, $\beta = 149.11°$) with some extra unreacted BCC ($Im3m$) Sn (simulated lattice parameter $a = 3.036$ Å), based on the Le Bail refinement. As seen in Fig.S1 of Supplementary Materials, the $Ama2$ SnH_4 can be excluded based on previous theoretical calculations, since it can only be stable up to 180 GPa and then transforms to $P6_3/mmc$ phase. The transition pressure will be much lower if considering the zero-energy effect. The Bragg position of $P6_3/mmc$ SnH_4 provided in Fig.S1 corresponds to the lattice parameters at 200 GPa, given in Ref. [16]. As can be seen, the $P6_3/mmc$ phase of SnH_4 can also be excluded given the poor matching between experimental data and the expected peak positions. In addition, the observed XRD peaks cannot be assigned to SnH_8 or SnH_{14} [18] neither. Due to the limited number of diffraction peaks and spotted diffraction pattern, we cannot perform structure refinement based on the $C2/m$ SnH_{12} structural model and further XRD experiment with larger sample or better statistics is required to get the accurate structrual parameters. It is noted that the stability pressure range for the SnH_{12} phase is lower than the prediction based on the harmonic approximation, which could overestimate the critical pressure for these phases [43,44]. Such an "overestimation" effect was also found in LaH_{10}; the experimental pressure to obtain LaH_{10} of ~ 150 GPa [25] is about 60 GPa lower than that (210 GPa) given by theoretical calculation [38].

Fig. 3 shows the temperature dependence of resistance $R(T)$ during the cooling and warming processes at a slow sweep rate of about 0.3 K/min. The data were measured in a DC current mode with a current of 0.05 mA. A metallic behavior was observed at high temperatures and the resistance undergoes a sudden drop starting at ~ 70 K upon cooling, implying the possible occurrence of superconductivity. The resistance decreases continuously below the transition but fails to reach zero at the lowest temperatures. This is presumably due to the insufficient reaction of Sn with hydrogen. During the warming-up process, the sudden jump of resistance is reproduced and shifts to ~74 K, confirming that it is an intrinsic property of the SnH_x sample. As noted previously [29], the observed thermal hysteresis between the cooling and warming processes is an artifact originating from the different location of temperature sensor with respect to the sample. Because the temperature sensor was attached to the stainless-steel frame of DAC, the measured temperature is always ahead of the actual sample temperature. Thus, the real T_c should be located in between 70 and

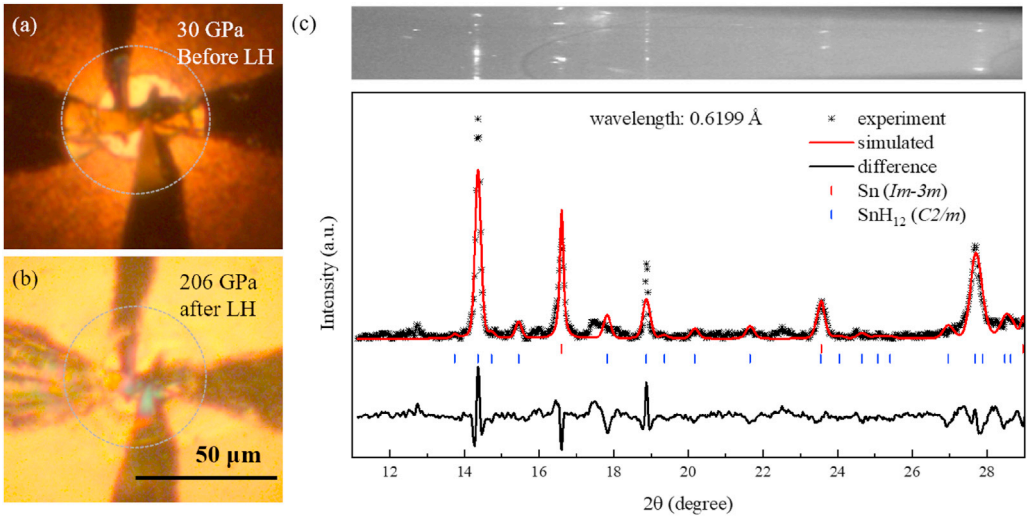

Fig. 2. (Color online) The photographs of sample inside DAC and synchrotron x-ray diffraction data for SnH_x sample at 206 GPa. (a, b) The optical photos of SnH_x sample before and after laser heating; the dotted circles indicate the approximated edge of culet; (c) x-ray diffraction data and Le Bail refinement result: upper panel, the original XRD data; lower panel, integrated XRD data and refinement with the Bragg positions of Sn and SnH_{12} [18].

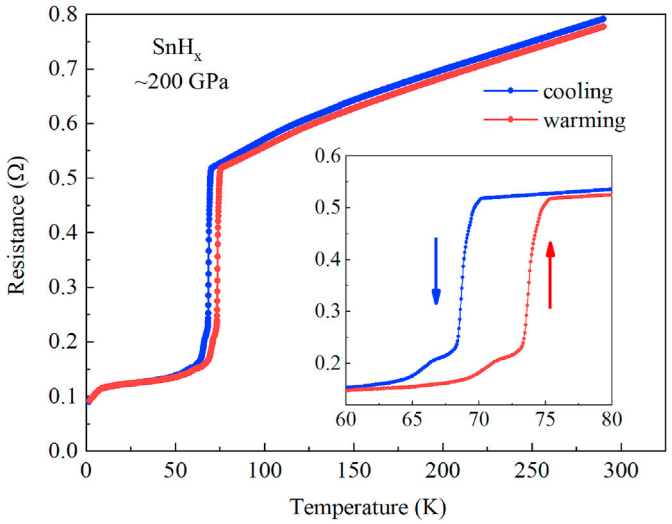

Fig. 3. (color online) *R-T* curve at ~ 200 GPa from 2 K to 290 K at zero field during the cooling (blue) and warming (red) processes. Inset shows the zoom-in region between 60 and 80 K.

74 K. In this case, we defined the T_c ~ 72 K as the average of 70 and 74 K. In addition to the sharp transition, we also reproducibly observed a second small step-like anomaly in $R(T)$ slightly below T_c. As discussed below, this second transition might arise from part of the sample with different hydrogen content.

To confirm the occurrence of superconductivity in SnH_x, we performed $R(T)$ measurements under different external magnetic fields. As seen clearly in Fig. 4(a), the resistance transition is shifted gradually to lower temperature upon applying magnetic fields, which is a hallmark of the superconducting transition. In addition, the superconducting transition is broadened up and the step-like anomalies become invisible with increasing fields. It is noted that the superconducting transition temperature decreases by 2-3 K at zero field in comparison with the data shown in Fig. 3. This should be ascribed to the pressure change after the first thermal cycling. Indeed, we confirmed that the pressure drops to ~190 GPa after the first resistance measurements shown in Fig. 3. But the pressure in DAC does not change any more after the first thermal cycling as checked after all the measurements in magnetic fields were finished.

As seen in Fig. 4(a), the effect of magnetic field on the superconducting transition is very strong; it is lowered by ~35 K under 7 T. To quantify the influence of magnetic field on T_c, here we determined the T_c value as the middle-point temperature of the resistance drop and plotted in Fig. 4(b) as a function of external fields. First, we can estimate the zero-temperature upper critical field $\mu_0 H_{c2}(0)$ by fitting the $\mu_0 H_{c2}(T)$ with the empirical Ginzburg–Landau (G-L) equation, viz. $\mu_0 H_{c2}(T) = \mu_0 H_{c2}(0)\,(1 - t^2)/(1 + t^2)$, where t is the reduced temperature T/T_c. As shown by the solid green curve in Fig. 4(b), the G-L fitting yields the $\mu_0 H_{c2}(0) = 11.2$ T and $T_c = 67.3$ K. The obtained $\mu_0 H_{c2}(0)$ is much smaller than the Pauli paramagnetic limited $\mu_0 H_p(0) = 1.84\ T_c \approx 122$ T, implying that the spin-paramagnetic effect is the major pair breaking mechanism. It is noteworthy that the ratio of $H_p(0)/H_{c2}(0)$ for SnH_{12} is considerably larger than the other known superhydrides superconductors and this issue deserves further investigations. Based on the obtained $\mu_0 H_{c2}(0)$, we can estimate the G-L coherent length $\xi = 5.4$ nm according to the formula $\xi = (\Phi_0/2\pi H_{c2}(0))^{1/2}$, where Φ_0 is the magnetic flux quantum. From the initial slope of $H_{c2}(T)$ at T_c, *i.e.* $dH_{c2}/dT|_{Tc} = -0.21$ T/K, we can also obtain the orbital limited $\mu_0 H_{c2}^{orb}(0) = -0.69 \times T_c \times dH_{c2}/dT|_{Tc} = 9.6$ T in the dirty limit of Werthamer–Helfand–Hohenberg (WHH) model without spin–orbit coupling [45]. Based on the simple models in Supplementary Materials, SnH_{12} obtained at 200 GPa and 1700 K could be a weak type-II superconductor.

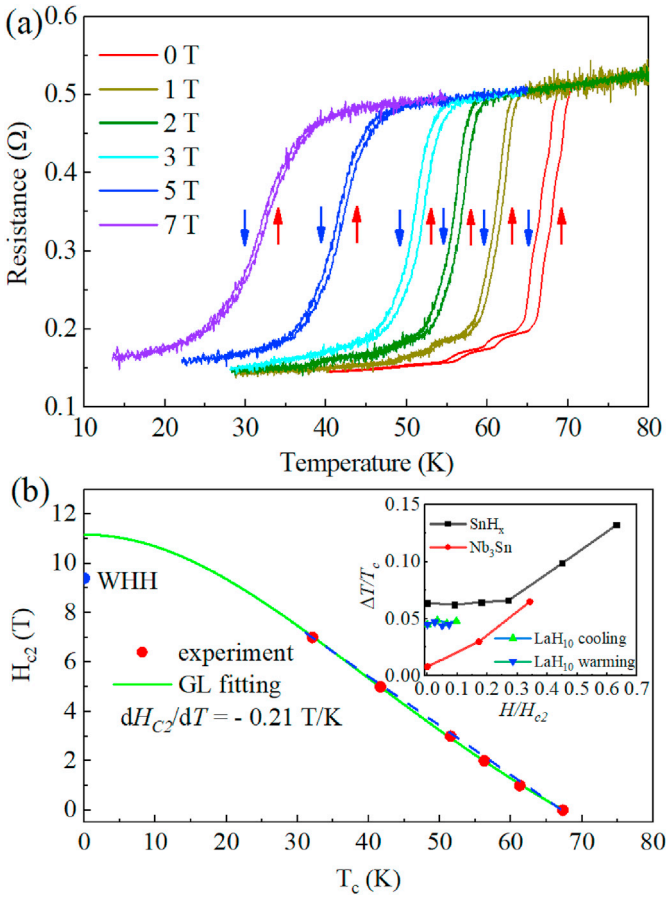

Fig. 4. (color online) Magnetic field effect on the superconducting transition of SnH_x at ~190 GPa. (a) temperature dependence of resistance near the superconducting transition under different magnetic fields; (b) Field dependence of the critical temperature fitted by the Ginzberg–Landau (green solid curve) and Werthamer–Helfand–Hohenberg (WHH) (blue dashed line) expressions; inset: the resistive broadening behavior in SnH_x, compared with "nonstandard" LaH_{10} [25] and standard Nb_3Sn [47].

Recently, J. E. Hirsch et al. raised an interesting issue that the hydride superconductors could be "nonstandard superconductors" due to the absence of superconducting transition broadening effect under magnetic fields [46]. It is noted that in those previous studies, the studied magnetic field range is only a small portion of the experimental upper critical field H_{c2}. Here, the much reduced $H_{c2}(0) = 11.2$ T in SnH_x enables us to examine this issue over a much wider range of H/H_{c2} even in the lab attainable field range. As seen in the inset of Fig. 4(b), the $\Delta T/T_c$ is quite flat for $H/H_{c2} < 0.3$, similar with that of LaH_{10} [25] and consistent with the claim of "nonstandard superconductors" [46], but the field-induced resistive broadening effect in SnH_x is quite obvious for $H/H_{c2} > 0.3$ and it follows the trend of traditional standard superconductor Nb_3Sn [47]. This indicates that the hydride superconductors should fall into the category of "standard superconductors" if the studied magnetic-field range is large enough. We also note a relatively larger initial $\Delta T/T_c$ in various hydride superconductors [46], which should be due to the relatively low phase impurity and large pressure gradient under megabar pressure. Such a large initial $\Delta T/T_c$ could blanket the broadening effect at low H/H_{c2} range.

The predicted T_c values for SnH_x by Esfahani et al. fall in the range of 81–97 K depending on the hydrogen content [18]. For *C*2/*m* SnH_{12}, its T_c is 93 K at 250 GPa in case of Coulomb pseudopotential $\mu^* = 0.1$. In our experiment, the observed T_c is about 72 K, which is ~21 K lower than the theoretical value, if we ignore the pressure effect. Similar situation also occurs in LaH_{10}, for which the predicted T_c is 286 K by using $\mu^* = 0.1$ [38] whereas the experimental T_c is 250–260 K [25,26,29]. For LaH_{10} with the clathrate structure, the H atoms are weakly bonded covalently with H–H distance of 1.08 Å at 200 GPa and the molecular H_2 unit is strongly suppressed [39]. The weak H–H interaction in LaH_{10} with large distance (comparable with the H–H distance in atomic metallic hydrogen at 500 GPa) is beneficial for the electron-phonon coupling (EPC) since all H vibrations are involved in the EPC process [39]. In contrast, SnH_{12} contains a substantial amount of H_2 and H_4 semi-molecule units as presented in Fig. 1(d), and the latter is formed by two H_2-groups with a distance about 0.99 Å at 250 GPa [18]. Hence, EPC effect in SnH_{12} is not as strong as that in LaH_{10}. In addition, SnH_{12} has less H-projected density of states at the Fermi level [18]. All these factors mentioned above determine the relatively low T_c of SnH_{12} in comparison with the LaH_{10}. According to the recent proposal by Sun et al. [48], if we can dope electrons into such hydrides and break the H_2/H_4 molecules, it is expected to enhance the T_c substantially, which makes SnH_x a promising parent compound for exploring novel ternary hydrides with higher T_c.

4. Conclusion

In summary, we have synthesized SnH_x sample by laser heating the Sn and ammonia borane inside a diamond anvil cell at ~200 GPa and ~1700 K. The obtained sample could be the theoretically predicted *C*2/*m* SnH_{12} with $T_c \approx 70$ K and a relatively low upper critical field $\mu_0 H_{c2}(0) = 11.2$ T by using the G-L fitting. The resistive broadening behavior in SnH_x follows the trend of traditional standard superconductors, which has an important implication for other hydride superconductors. SnH_{12} could be a promising parent compound for exploring novel electron-doped ternary hydrides with higher T_c, and it is also the first HTS in IVA-group hydrides.

Author contributions

F. Hong, X. H. Yu and J. G. Cheng conceived this research. J. G. Cheng and Z. X. Zhao supervised the project. F. Hong prepared the experiment and loaded the DAC sample. X. H. Yu and L. X. Yang did the laser heating. P. F. Shan, P. T. Yang, Z. Y. Liu, J .P. Sun did the low-temperature resistance measurement. F. Hong, B. B. Yue did the synchrotron x-ray diffraction, and J. H. Dai, Y. Y. Yin, H. Yu. joined the synchrotron experiment. F. Hong, P. F. Shan prepared the original manuscript draft, X. H. Yu and J. G. Cheng made further revision. All authors discussed the results and made comments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtphys.2021.100596.

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