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Superconductivity of platinum hydride

Takahiro Matsuoka,[1,*] Masahiro Hishida,[2] Keiji Kuno,[3] Naohisa Hirao,[4] Yasuo Ohishi,[4]
Shigeo Sasaki,[1] Kazushi Takahama,[5] and Katsuya Shimizu[5]
[1]*Department of Electrical, Electronic and Computer Engineering, Faculty of Engineering, Gifu University, Gifu 501-1193, Japan*
[2]*Department of Materials Science and Technology, Gifu University, Gifu 501-1193, Japan*
[3]*Environmental and Renewable Energy Systems Division, Gifu University, Gifu 501-1193, Japan*
[4]*Japan Synchrotron Radiation Research Institute (JASRI), Hyogo 679-5198, Japan*
[5]*Center for Science and Technology under Extreme Conditions, Graduate School of Engineering Science,*
Osaka University, Osaka 560-8531, Japan

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We report the ac magnetic susceptibility, electrical resistance, and x-ray diffraction measurements of PtH_x ($x \simeq 1$) in diamond anvil cells, that reveal the superconducting transition. At 30 GPa, when PtH_x is in a $P6_3/mmc$ structure, PtH_x exhibits the superconducting transition at 7 K. Remarkably, the observed T_c is higher than that of powdered Pt by more than three orders of magnitude. It is suggested that the noble metals in the periodic table of elements possibly form a region where hydrides have higher T_c than elements.

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I. INTRODUCTION

Pt, a well known chemically inert noble metal, has a strong electron-phonon (e-p) coupling, which is favorable for superconductivity [1–3]. On the other hand, its mass magnetic susceptibility 1.21×10^{-8} (m^3/kg in SI units) is one of the largest ones among the metals which do not show magnetic ordering [1,2]. Consequently, the $5d$ conduction electrons of Pt show strong spin fluctuations on short length and time scales which tend to suppress the superconducting transition [3]. This large paramagnetic Pauli susceptibility also enhances the effective moments of magnetic $3d$ impurities (e.g., Fe, Mn, Co) because of the polarization of the neighboring $5d$ conduction electrons of the host metal [4]. To the best of our knowledge, there has been no report that bulk Pt exhibits a superconducting transition at either ambient or high pressures. In the quest for high-temperature superconductivity, it is natural to wonder how we can make a new superconductor that has a superconducting transition temperature (T_c) as high as possible from this noble metal. The magnetic studies by König *et al.* have found that powder Pt with an average grain size about 2 μm showed a magnetic behavior very different from a bulk material: powder Pt shows a much weaker temperature dependence of the dynamic susceptibility in the mK and μK region [5]. Then, the superconducting transition was observed at $T_c = 0.62$–1.38 mK [5]. The lattice softening and the enhanced e-p coupling as a result of a large surface-to-volume ratio have been suggested to play roles in the superconductivity of powdered Pt [5,6].

To manipulate the electronic states of metals, hydrogenation sometimes is an effective means. A good example is palladium hydride (PdH_x). Pd has a large mass magnetic susceptibility $+6.57 \times 10^{-8}$ (m^3/kg in SI units) and is paramagnetic [1]. The superconductivity of Pd has not been detected down to 2×10^{-4} K at 1 bar [1]. When it forms a hydride PdH_x which has a NaCl-type crystal structure, the s electrons provided from H atoms occupy the $1s$-$4d$ bonding band and unoccupied d band of Pd [7,8]. This Pd $4d$ and H $1s$ electron hybridization results in the reduction of electron density of states (e-DOS) at the Fermi level (E_F), hence the loss of paramagnetic susceptibility. PdH_x becomes non-magnetic with hydrogen composition $x = \mathrm{H}/\mathrm{Pd}$ larger than 0.62 [9,10]. At the same time, the coupling between conduction electrons and soft-optic-mode that is related to local hydrogen vibrations is enhanced [7,8]. As a result, the superconductivity of PdH_x appears at 1 K for $x \sim 0.8$, and the T_c increases to 9 K as x increases to 1 [11,12]. The electronic band structures of elemental Pt and Pd share similar features: the broad dispersion bands of the $5d$ and $4d$ electrons crossing the E_F and the large e-DOS at E_F [13]. In PtH, hybridization between Pt $5d$ and H $1s$ [7,14] and the resulting strengthened e-p coupling are anticipated [7,14–17]. Also, this hybridization could lead to the reduction of e-DOS at E_F and the loss of magnetic susceptibility. Theoretical calculations have predicted T_c at a temperature of 10–25 K [7,14–17]. It is noted that the predicted T_c is suppressed to below 0.4 K when anharmonic effects, which often have a considerable degree of importance to the physical properties of hydrogen-rich compounds, are included in the calculation [18]. Although Pt does not react with H_2 at ambient pressure, recent x-ray diffraction (XRD) experiments have revealed the formation of PtH_x ($x \sim 1$) in high-pressure H_2 above 27 GPa at room temperature [15,19]. This compound exhibits two phases, named PtH-I and PtH-II respectively, coexisting up to 42 GPa at room temperature, above which the single phase of PtH-II exists [15,19]. The crystal structure of PtH-I is complicated, and $P321$ is suggested in which H atoms occupy

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[*] Present address: Joint Institute for Advanced Materials (JIAM), The University of Tennessee, Knoxville, Tennessee 37996, USA; TKMatsuoka08@gmail.com/tmatsuok@utk.edu

tetrahedral interstitial sites [15]. In PtH-II, Pt atoms form a hexagonal close-packed lattice ($P6_3/mmc$), and H atoms are predicted to be in the octahedral interstitial sites [15,19].

In this paper, we report the measurements of the ac-magnetic susceptibility, electrical resistance, and XRD of PtH_x in diamond anvil cells (DACs). Above 30 GPa, PtH-II exhibits a superconducting transition. It is thought that PtH-I does not show superconductivity above 4 K. Remarkably, the T_c (7 K at 30 GPa) of PtH-II is higher than that of powdered Pt by three orders of magnitude. It is suggested that the noble metal group in the periodic table of elements forms a spot where their hydrides have higher T_c than the elements.

II. EXPERIMENTAL

The starting material for the synthesis of PtH_x is a piece of Pt foil (Nilaco, 99.95%). In previous studies, PtH was synthesized by compressing a Pt-H_2 mixture using a diamond anvil cell (DAC) to pressures above 25 GPa at room temperature [15,19]. However, the electrical resistance measurements in a fluid or solid H_2 pressure transmitting medium are extremely challenging. Since H_2 is highly compressible, the sample chamber significantly shrinks under compression, destroying the sample and electrodes. In the present experiments, instead of pure H_2, we employed the borane-ammonia complex NH_3BH_3 (SIGMA-ALDRICH, 97%) as an H_2 source [20,21]. At 1 bar, NH_3BH_3 releases H_2 on heating, and it ultimately decomposes to cubic boron nitride (c-BN) and H_2 at 1000 K. We found that NH_3BH_3 released H_2 even at pressures as high as 30 GPa by heating to sufficiently high temperatures near 1800 K, and PtH-II could be formed (Fig. 1). In the present experiments, Pt foil was sandwiched between the NH_3BH_3 powders and compressed to the pressures above 30 GPa at room temperature. Then, Pt and NH_3BH_3 were heated by focusing an IR laser ($\lambda = 1070$ nm, SPI-laser) on the sample Pt. We prepared three samples using the same method for ac magnetic susceptibility (sample 1) and electrical resistance (samples 2 and 3) measurements. In the electrical resistance measurements, we compressed gold wires (Au electrodes) and NaCl thin plates (thermal insulation between samples and a diamond anvil) together with the samples. The ac magnetic susceptibility measurements were performed using a pickup coil, a compensation coil, and an excitation (ac magnetic field application) coil placed around a gasket. The superconducting transition was detected by observing the change of electromagnetic force induced in a pick-up coil (see Fig. s1 in the Supplemental Material [22] and Refs. [23,24] for further details). Figure 1(a) shows the typical

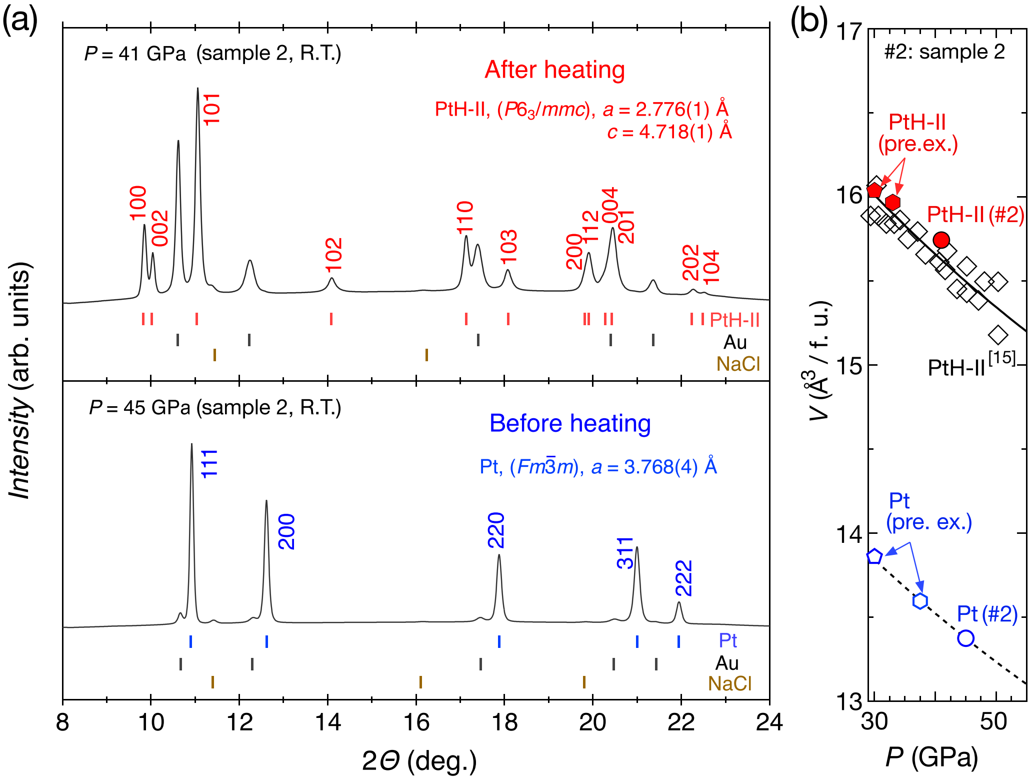

FIG. 1. Synthesis of PtH_x ($x \simeq 1$). (a) XRD profiles of sample 2 before and after the synthesis of PtH_x. The *in situ* XRD measurements were performed at the SPring-8/BL10XU beamline using a monochromatic synchrotron x-ray beam ($\lambda = 0.4145$ Å). Vertical bars indicate the diffraction peak positions of PtH-II ($P6_3/mmc$), Pt ($Fm\bar{3}m$), Au ($Fm\bar{3}m$, electrodes), and NaCl (CsCl-type, thermal insulation between a diamond anvil and the sample) at 45 and 41 GPa. The smooth and broad backgrounds in the XRD profiles are from Compton scattering of a diamond anvil. The diffractions from NH_3BH_3 and c-BN are weak and barely visible in the XRD profiles shown here. (b) V ($\mathrm{Å}^3$/f.u.) vs P for Pt and PtH-II. An open and a filled circle show the data of sample 2 before (Pt) and after (PtH-II) laser heating, respectively. In the same manner, the open and filled pentagons and hexagons show the data obtained in two independent preliminary experiments (pre.ex.). The open diamonds are the reported data for PtH-II synthesized in excess H_2 at room temperature [15]. The solid and dashed lines are EOS of PtH-II and Pt [15,29,30].

synchrotron XRD profiles of sample 2 at room temperature before and after the laser heating. The volume per formula unit [V (Å^3/f.u.)] of Pt (before heating) and PtH-II (after heating) are plotted as a function of pressure. The crystal structure and lattice parameters [$P6_3/mmc$, $a = 2.776(1)$ Å, $c = 4.718(1)$ Å at 41 GPa] of sample 2 after laser heating showed excellent agreement with those of PtH-II synthesized in high-pressure H_2 at room temperature [15,19]. Besides, the lattice parameters of PtH-II heated in excess H_2 at 41 GPa was in good agreement with the previously reported data [15,19] of PtH-II formed in excess H_2 at room temperature (see Fig. s2 in the Supplemental Material [22]). By these observations, it is thought that laser heating does not affect the crystal structure of PtH, and the PtH$_x$ synthesized in heated NH_3BH_3 has the same or similar hydrogen content $x = H/Pt$ as PtH. Therefore, we assume that the x of our PtH$_x$ samples are 1 or almost 1. Here we note that our XRD measurements confirmed that the formations of platinum nitride (PtN, zinc-blende structure) [25], gold hydride (see also Fig. s3 in the Supplemental Material [22]), and Na_3Cl and $NaCl_3$ [26] did not occur (Fig. 1). In addition, it is empirically known that elemental Au does not exhibit superconductivity at least at the pressures and temperatures of the present experiments. Thus, in the sample chamber, there was no possible material that contributed the observed superconductivity, except for PtH$_x$. It is also noted that the synthesized PtH$_x$ sample was maintained for at least 12 hours at room temperature without decomposition after its synthesis (see Fig. s4 in the Supplemental Material [22]). The pressure was determined by using the shift of the first-order Raman band spectra of the diamond anvil facing the sample, with a proposed calibration [27]. The temperature during the laser heating was estimated by collecting thermal radiation from the sample and analyzing it in a wavelength between 600 and 800 nm to convert to the temperature in accordance with Planck's blackbody radiation law [28]. The indicated pressures for electrical resistance and ac magnetic susceptibility measurements were that obtained by averaging the values obtained at room temperature before and after each cooling and warming cycle. The actual pressures at low temperatures are thought to be somewhat different from the indicated values.

III. RESULTS

Figure 2 shows the temperature dependence of the real part of the ac magnetic susceptibility (χ') of PtH$_x$ (sample 1) at different pressures. We performed the measurements upon pressure decrease at 36, 32, and 28 GPa. The sharp drop of χ' appears at 36 and 32 GPa at 4.8 and 6.7 K, respectively. Using the analysis discussed in detail [22,31,32], the observed $\Delta\chi\prime = 6$–11 nV jump at T_c is consistent with perfect diamagnetism, suggesting that whole sample exhibits superconductivity. At 28 GPa, near the pressure where the PtH$_x$ transforms from PtH-II to PtH-I upon pressure decrease, no diamagnetic signal is visible above 4.6 K [15]. It is thought that PtH-I is the majority in sample 1 at 28 GPa, and the superconducting transition vanished for temperatures above 4.6 K. Then, we conclude that the observed superconducting transitions at 32 and 36 GPa are from PtH-II.

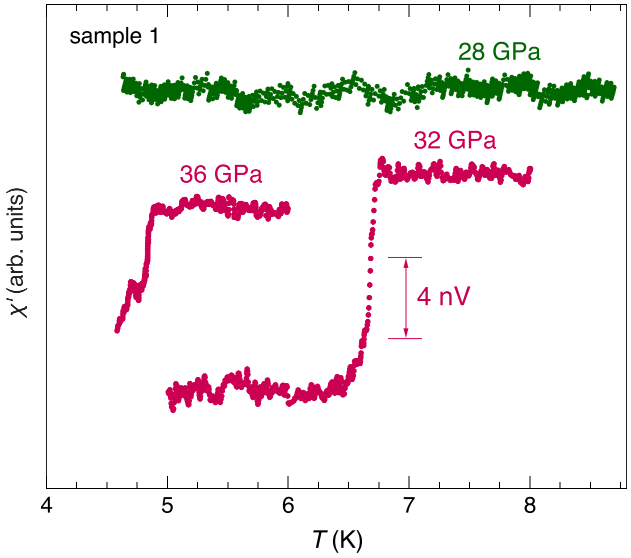

FIG. 2. χ' vs T for PtH$_x$ ($x \simeq 1$) as pressure is decreased from 36 to 28 GPa. The superconducting transition shifts under decreasing pressure to higher temperatures. No superconducting transition was observed at 28 GPa. T_c is determined from the temperature at the transition onset. All data are on the same scale but are shifted vertically.

To obtain further evidence of the superconductivity, we performed the electrical resistance measurements of PtH-II (samples 2 and 3). Figures 3(a) and 3(b) show the temperature dependence of the electrical resistance (R) of PtH-II at 35 GPa (sample 2). In Fig. 3(a), the R vs T curve has a positive slope at temperatures below 300 K, clearly indicating that PtH-II is a metal. At 7.5 K, R exhibits a sharp decrease, deviating from the linear dependence on the temperature. To investigate the origin of the reduction of R, we performed the

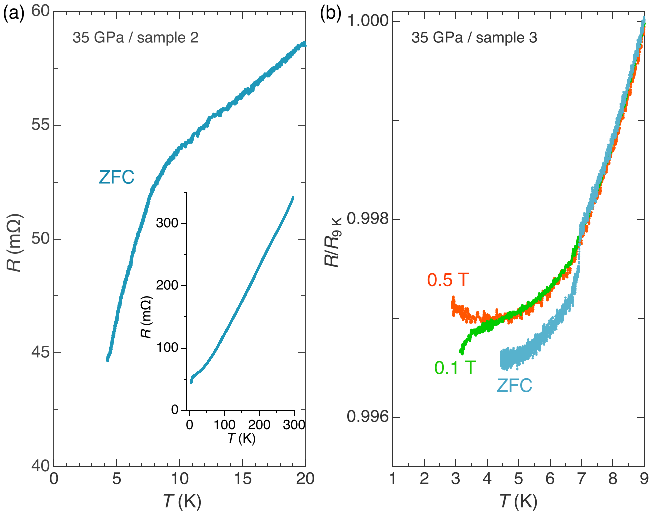

FIG. 3. R vs T of PtH$_x$ ($x \simeq 1$) at 35 GPa in external magnetic fields. (a) R vs T curve of sample 2 (PtH-II) at 35 GPa in zero-magnetic-field cooling (ZFC). The inset graph indicates the data from 4.2 to 300 K. (b) R vs T curves of sample 3 (PtH-II) at 35 GPa in 0 T (ZFC), 0.1 T, and 0.5 T field cooled (FC). The R data were scaled at 9 K for comparison.

electrical resistance measurements on sample 3 at 35 GPa in an external magnetic field [Fig. 3(b)]. In the zero-field-cooled (ZFC) measurement at 35 GPa, the R shows a sharp drop at 7 K, in agreement with sample 2. When a magnetic field $H = 0.1$ T is applied, the decline of R shifts to 3.5 K and it vanishes for temperature above 2.8 K at $H = 0.5$ T. Since the shift of T_c to lower temperatures in an external magnetic field is one of the characteristics of superconductivity, the observed shift of the resistance drop temperature strongly suggests the superconducting transition of PtH-II. Regarding the electrical resistance measurements, we note the following points. The electrical resistance measurements of sample 2 were performed by a two-point contact method due to technical difficulties. Each Au electrode was divided into two wires in the vicinity of the samples [22]. In the experiments of sample 3, although a four-point contact method was implemented, one of four electrodes (V2 in Fig. s1(b) of the Supplemental Material [22]) was broken, and the electrode (I2 in Fig. s1(b) of the Supplemental Material [22]) was divided into two outside of a DAC using copper (Cu) wires. Therefore, the measured R includes the contact resistance between electrodes and samples, and the resistance of electrodes. In addition, it is thought that a pressure gradient across the samples exists at high pressures. Consequently, the R of samples 2 and 3 do not drop to zero at a T_c and the transition becomes broad. The critical magnetic filed (H_c) is estimated to be very small if we use the data shown in Fig. 3. However, since the body of the DAC and the gasket were not completely nonmagnetic at low temperatures, there is a possibility that the actual magnetic flux on the sample was bigger than the indicated values. We leave the investigation of the H_c to future studies.

Taking the data together, the present experiments provide unambiguous evidence for the superconductivity of PtH-II. Remarkably, the observed T_c of PtH-II is more than three orders of magnitude larger than that of compacted-powder Pt [5].

IV. DISCUSSIONS AND CONCLUSION

For discussion, we compare the experimental results with theoretical predictions. In Fig. 4, the T_c of sample 1 (ac magnetic susceptibility measurements) is plotted as a function of pressure together with the predicted T_c's and structural phase diagrams [15,16,19]. Since the pressures at the T_c's could not be measured, we avoid plotting the T_c's obtained for different samples (1–3) in the same graph. The present experiments agree with theoretical predictions at the point that PtH-II is a superconductor. On the other hand, the observed T_c's are almost half of the ones suggested by the calculations based on a harmonic approximation. Furthermore, the observed T_c's are much higher than 0.4 K by a calculation that takes account of anharmonic effects [18]. The reason for the discrepancies is unknown at the current moment. In PdH$_x$, it has been observed that the T_c increases proportionally to the hydrogen content x = H/Pd in PdH$_x$ [11,12]. Although we assume that the x of our PtH$_x$ samples are almost 1, there is no measure to count the number of x precisely at high pressures such as 35 GPa with currently available experimental techniques. If the observed T_c is for PtH$_x$ with x less than 1, and the x critically affects the T_c, there would be some more chance to obtain higher T_c by improving the stoichiometry. Such studies, combining the observation of the isotope effect on the T_c of PtD, would also advance our understanding of superconductivity in metal hydrides and point out the way to obtain new superconductors.

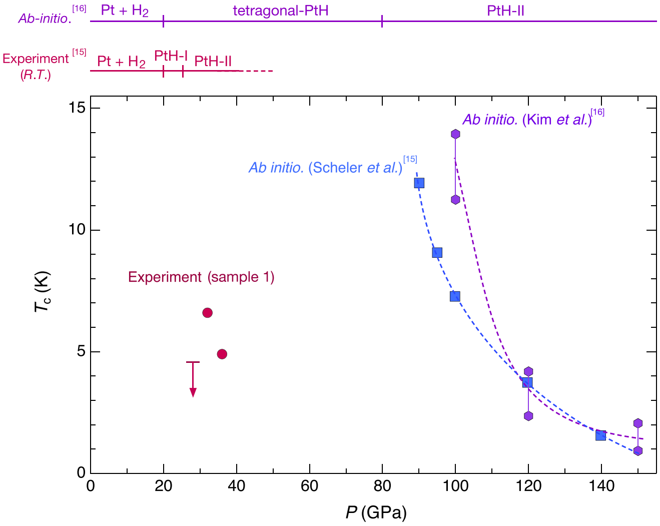

FIG. 4. T_c vs P for PtH$_x$ ($x \simeq 1$). The filled circle show the T_c of sample 1. The down arrow at 28 GPa indicates that the superconducting transition is not observed above 4.6 K. The rectangles and hexagons are predicted T_c by *ab initio* calculations [15,16]. Dashed curves are guides for the eyes. The horizontal solid and dotted lines placed above the graph indicate the structural phase boundaries observed in the experiments and predicted by an *ab initio* calculation [15,16], respectively. Both *ab initio* calculations of Refs. [15,16] predict that PtH-II is stable at pressures above 80 GPa.

In most superconducting d -metals, the presence of hydrogen in the metal lattice either decreases the T_c (e.g., TcH, ReH$_x$, VH, NbH, ZrD$_x$) or does not affect it (e.g., RuH, MoH) [33–35]. Among the transition metal hydrides synthesized so far, PdH and PtH are the only materials that have higher T_c than elemental metals [11,12,36–42]. The *ab initio* calculation by Kim *et. al.* has predicted the formation of AuH, silver hydride (AgH), rhodium hydride (RhH), and iridium hydride (IrH)$_8$ under high pressures. For all of them, except AgH, superconductivity has been predicted [16]. In the periodic table of elements, these noble metals possibly form a spot where their hydrides exhibit superconductivity at higher temperatures than elements. Although RhH does not exhibit a superconducting transition down to 0.3K at ambient pressure, it would be worth extending the search to high pressures [33].

In summary, we have revealed the superconducting transition of PtH-II by the ac magnetic susceptibility, electrical resistance, and XRD measurements under high pressures. The T_c of PtH-II is 7 K at 30 GPa. The present results provide a definitive answer to the question of whether we can make a superconductor from Pt and H. Similarly to the case of PdH, the observed highest T_c of PtH-II is more than 10^3 times higher than that of powder Pt [5,11,12]. The observation of the superconductivity in PtH-II stimulates interest in other noble metal hydrides because they possibly form a group whose metal hydrides have higher T_c than that of elemental metals. Finally, the present experiments have an importance to the field of high-pressure science. Pt has been widely used in high-pressure experiments as a pressure calibrant, for electrical probes, and as a heat absorber. Also, in the studies of several hydrides, for example, Pt has been used for electrical probes [43,44]. After the findings of the decomposition of SiH_4, there have been arguments that the reported superconducting transition of compressed SiH_4 was actually from PtH formed in Pt electrodes by the H_2 from decomposed SiH_4 [43,45]. The present study does not give the argument a clear answer because the pressure range of the study is far below that of the experiments for SiH_4. However, with the growing interest in high-temperature superconducting metal hydrides, the results advise us to avoid the usage of Pt as an electrode which contacts with hydrogen, hydrides, and other hydrogen containing materials.

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