Stoichiometric evolutions of PH$_3$ under high pressure: implication for high-$T_c$ superconducting hydrides

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ABSTRACT

The superconductivity of hydrides under high pressure has attracted a great deal of attention since the recent observation of the superconducting transition at 203 K in strongly compressed H$_2$S. It has been realized that the stoichiometry of hydrides might change under high pressure, which is crucial in understanding the superconducting mechanism. In this study, PH$_3$ was studied to understand its superconducting transition and stoichiometry under high pressure using Raman, IR and X-ray diffraction measurements, as well as theoretical calculations. PH$_3$ is stable below 11.7 GPa and then it starts to dehydrogenate through two dimerization processes at room temperature and pressures up to 25 GPa. Two resulting phosphorus hydrides, P$_2$H$_4$ and P$_4$H$_6$, were verified experimentally and can be recovered to ambient pressure. Under further compression above 35 GPa, the P$_4$H$_6$ directly decomposed into elemental phosphorus. Low temperature can greatly hinder polymerization/decomposition under high pressure and retains P$_4$H$_6$ up to at least 205 GPa. The superconductivity transition temperature of P$_4$H$_6$ is predicted to be 67 K at 200 GPa, which agrees with the reported result, suggesting that it might be responsible for superconductivity at higher pressures. Our results clearly show that P$_2$H$_4$ and P$_4$H$_6$ are the only stable P–H compounds between PH$_3$ and elemental phosphorus, which is helpful for shedding light on the superconducting mechanism.

Keywords: high pressure, hydrides, superconductivity, stoichiometric evolution

INTRODUCTION

Since superconducting mercury was first reported [1,2], scientists have continued to search for new high critical temperature ($T_c$) materials. In 2004, Ashcroft studied hydrogen-dominant hydrides [3], in which condensed H$_2$ may contribute to a high $T_c$. Motivated by this work, extensive theoretical investigations on this system have been reported, such as SiH$_4$ [4], GeH$_4$ [5], GaH$_3$ [6], SiH$_4$(H$_2$)$_2$ [7], CaH$_6$ [8] and YH$_6$ [9], etc. A few remarkable high-$T_c$ materials have also been observed in subsequent experimental studies. Recently, Drozdov et al. reported the superconductive transition of H$_2$S at 203 K and 155 GPa [10], which broke the highest $T_c$ record [11]. Many theoretical [12,13] and experimental [14] studies have explored its stoichiometry and structure, which play an important role in understanding the underlying mechanism of superconductivity.

Very recently, PH$_3$, a typical hydrogen-rich hydride, has attracted a great deal of research interest because of its superconducting transition discovered by Drozdov and his co-workers [15–20]. Their experimental work revealed that PH$_3$ might be a high-temperature superconducting candidate. From the resistance measurements, a superconducting transitionsignature was observed at $T_c$ of 30 K. This increased to 103 K with pressures up to 207 GPa. However, structural information was not provided, and the origin of the superconducting transition remains puzzling. Subsequent theoretical studies [16–19] showed that the P–H compound should also be a complex system, and all the predicted structures were metastable with respect to the elemental phase.

Flores-Livas et al. [16] studied the phase diagram of phosphorus hydrides with different stoichiometries and found that they tended to decompose into phosphorus and hydrogen at high pressure.
Liu et al. [17] predicted a PH3 phase with a monoclinic structure (C2/m) and a Tc of 83 K at 200 GPa, which is closer to the observed superconducting transition temperature. Shamp et al. [18] predicted that PH3 is thermodynamically unstable during decomposition into the elemental phases, as well as PH2 and H2. Two PH2 phases with C2/m and I4/mmm symmetry were computed as metastable at 200 GPa. The corresponding superconducting critical temperatures were 76 and 70 K, respectively. Bi et al. [19] found that a dynamically stable PH2 phase was the best according to the observed superconducting transition at 80 GPa. The PH3 phase to PH2 phase reaction was exothermic at that pressure, which proves the spontaneity of the reaction.

Until now, the PH3 phase under compression has remained unknown and no relevant experimental studies have been reported. The high-pressure stoichiometry and structural behavior of PH3 are critical to understanding the superconducting transition in the P–H system, which needs to be experimentally determined. For this purpose, we studied the structural behavior of PH3 under high pressure. We identified the pressure-induced step-by-step polymerization of PH3 and a route to elemental phosphorus that unveiled the unknown transition process and provides experimental evidence for understanding the underlying mechanism of the superconductivity of P–H compounds.

RESULTS AND DISCUSSION
Stoichiometric evolutions of PH3 at room temperature

After the PH3 gas was loaded into the sample chamber of the diamond anvil cell (DAC) and returned to room temperature, a colorless and transparent sample (Supplementary Fig. 1, available as Supplementary Data at NSR online) was observed. The characteristic Raman peaks (Supplementary Fig. 1, available as Supplementary Data at NSR online) at 978 (υ2, symmetric bending mode), 1104 (υ4, asymmetric bending mode), 2317 (υ1, stretching mode) and 2331 (υ3, stretching mode; shoulder) cm⁻¹ agreed well with previous reports [21], indicating the existence of PH3 in the chamber.

The X-rays can damage the sample (Supplementary Fig. 2, available as Supplementary Data at NSR online), so Raman and infrared absorption spectroscopy (IR) were mainly used for our in situ studies of PH3 at high pressure. Figure 1a and c shows the Raman spectra of the sample during compression. Under high pressure, these characteristic modes blue shifted and broadened (Fig. 1b and d) and eventually vanished at 20.5 GPa. Several new peaks (marked by black asterisks and arrows in Fig. 1a) were observed at around 11.7 GPa, which suggested a phase transition. For the P–H stretching modes, we also noticed a dramatic expansion of the characteristic bonds. Figure 1d shows the peak positions of the υ1 and υ3 modes as a function of pressure. The peak shift of υ1 dramatically decreased and started to red shift at 11.7 GPa. We attributed these changes to a transition in the sample near 11.7 GPa.

These new peaks in the Raman spectra (Fig. 1a) were consistent with previous studies about P2H4 at ambient pressure. The two new peaks at low frequencies correspond to the PH2 rocking mode and P–P stretching mode in the P2H4 molecule, which were observed at around 217 and 436 cm⁻¹, respectively [22,23]. The emergency P–P bond at 11.7 GPa proved the dimerization of PH3 molecules. The other new peaks at 1007 and 1093 cm⁻¹ were from the PH2 scissoring modes in the P2H4 molecule, which also agrees with previous reports. These factors suggest that the pressure-induced transition is due to the dimerization of PH3 at high pressure.

To verify the dimerization, we also studied the decompressed sample. A liquid sample was obtained after quenching to ambient conditions, as shown in the microphotograph of the decompressed sample (inset optical images in Fig. 2a). It is well known that P2H4 is a liquid at ambient pressure [22,24], which confirms that pressure drives the dimerization of PH3 to form P2H4 via this reaction:

$$2\text{PH}_3 \rightarrow \text{P}_2\text{H}_4 + \text{H}_2.$$  \hspace{1cm} (1)

We further employed Raman to measure the recovered liquid sample. However, after laser irradiation, the liquid sample decomposed and generated Hitdorf’s phosphorus [25,26] (Fig. 2a) according to the photodecomposition properties of P2H4 [24]. This offers more evidence of our findings.

We also employed IR to trace the in situ information of the new product at high pressure. Supplementary Fig. 3a, available as Supplementary Data at NSR online, shows the IR peak near 1095 cm⁻¹ broadened and shifted slightly to a lower frequency with increasing pressure, but an obvious new shoulder was observed at around 1058 cm⁻¹ after decompressing the sample to 11.8 GPa (Supplementary Fig. 3c and d, available as Supplementary Data at NSR online). This new shoulder matched the P2H4 scissors mode well, which was observed at around 1052 cm⁻¹ in a solid state at ambient pressure [27]. This characteristic mode confirms the existence of P2H4. In addition to the P–H stretching modes in the IR spectra (Supplementary Fig. 3b, available as
Supplementary Data at NSR online), a new shoulder at around 2329 cm$^{-1}$ was observed, and it became stronger and stronger with increasing pressure. After it had quenched to 11.8 GPa, the new shoulder peak was more obvious compared to the IR spectrum measured at 12 GPa during compression. This proves dimerization.

As the pressure increased, the P$_2$H$_4$ showed piezochromism. It became yellow, then red and darkened, and eventually became opaque at pressures higher than 25 GPa, consistently with the observations of Drozdov et al. at low temperatures (180 K). As the sample became totally opaque, the vibrational signal vanished and hindered the in situ high-pressure vibrational spectra measurement. Therefore, we had to quench the sample to ambient conditions from different pressures (25 and 35 GPa) and employed Raman spectroscopy to investigate the different quenched residues. Interestingly, once the sample became completely opaque above 25 GPa, it maintained its opaque solid state even when decompressed to room pressure. This irreversible process suggests that a new transition occurred at higher pressures.

Figure 2b shows that the Raman spectrum of the residue quenched from 25 GPa after the opaque transition. A weak peak near 873 cm$^{-1}$ belonging to PH$_3$ twisting and a strong peak at 2248.5 cm$^{-1}$ belonging to P–H stretching exist in the spectrum. This new P–H stretching peak is located at a much lower wave number than in PH$_3$, P$_2$H$_4$ ($\sim$2292 cm$^{-1}$) and P$_3$H$_5$ ($\sim$2267 cm$^{-1}$) [24], suggesting that the residue contained a new kind of phosphorus hydride. Figure 2c shows the P–H stretching mode of P$_n$H$_{n+2}$ shifts to lower frequency as $n$ becomes larger. Following this trend, we deduced that the new phosphorus hydride was P$_3$H$_6$, which suggests that the P$_2$H$_4$ molecules continued to dimerize and form P$_3$H$_6$ at higher pressure.

To confirm the second dimerization, we calculated the Raman modes of P$_n$H$_{n+2}$ using the Gaussian 09 program at the B3LYP/6–311(d, p) level [28]. Supplementary Table 1, available as Supplementary Data at NSR online, shows the calculated Raman modes of two typical P$_n$H$_{n+2}$ conformers, in which the four phosphorus atoms are linear and U-type (Supplementary Fig. 4a and b, available as Supplementary Data at NSR online). The calculated Raman spectra show that they both have four characteristic bands corresponding to the stretching vibration (350–450 cm$^{-1}$) of the P–P bond, twisting vibration (700–900 cm$^{-1}$) of the PH$_2$ group, scissoring vibration ($\sim$1070 cm$^{-1}$) of the PH$_3$ group and stretching vibration of the P–H bond, respectively. Moreover, the P–H stretching mode can further shift to a lower frequency (2278 cm$^{-1}$).
From Supplementary Table 1, available as Supplementary Data at NSR online, we can see that the P–P stretching bonds and the twisting vibration of the PH2 group from linear P4H6 are closer to our observed peak, suggesting that the linear type P3H6 is the more possible conformer in the residue.

Besides the peaks from P3H6, several other obvious characteristic modes (123.8, 184.8, 218.9, 285, 357.2, 386.5, 407.7, 443.2 and 505.8 cm⁻¹) were observed below 550 cm⁻¹. These peaks are similar to fibrous red phosphorus characteristic modes [25,26], which indicated that parts of P3H6 were thoroughly dissociated when exposed to laser or decompression. At ambient pressure, phosphorus hydrides often undergo disproportionation into phosphorus-rich phosphanes upon exposure to light and heat [24]. However, we did not observe the Raman peaks from other phosphanes from the residue, which proves that P3H4 dimerized directly into P3H6 at high pressure, corresponding to this equation:

\[ 2P_3H_4 \rightarrow P_3H_6 + H_2. \]  \hspace{1cm} (2)

From the recovered sample, it is confirmed that P2H4 dimerizes at high pressure. However, as both Raman and IR signal disappeared at above 20 GPa, we could not get in situ high-pressure vibrational modes. Therefore, it might be possible that other compounds generated at high pressure, such as P4H6·H2, which may easily decompose back to P4H6 and H2 upon decompression.

Figure 2d shows that the Raman spectra of the residue quenched from 35 GPa. After decompression to 1 atm, typical black phosphorus modes were observed [29,30]. Therefore, P4H6 eventually decomposed into elemental phosphorus at 35 GPa. Hence, the corresponding reaction is as follows:

\[ P_4H_6 \rightarrow 4P + 3H_2. \]  \hspace{1cm} (3)

From the in situ high-pressure XRD (Fig. 2d), the typical diffraction rings of cubic phosphorus further confirmed the thorough decomposition of P4H6 at high pressure.
Figure 3. (a) The Raman spectrum of the sample quenched from 31 GPa. The inset image shows the photo-induced transition after laser irradiation. (b) The Raman spectra of the sample collected during decompression from 102 GPa. (c) The Raman spectra of the residue quenched from 205 (blue line) and 102 (red line) GPa, respectively. (d) The phase diagrams of PH₃ at room temperature and low temperature.

Stoichiometric evolutions of PH₃ at low temperature

The superconductivity of elemental phosphorus has already been studied both experimentally and theoretically [31–33]. The maximum $T_c$ is about 9.5 K at 32 GPa before it decreases with pressure. Near 100 GPa, the $T_c$ is about 4.3 K at 160 GPa, and no superconducting transition was detected in the temperature range from 4 to 40 K. The much lower $T_c$ of phosphorus compared to 100 K indicates that PH₃ or other phosphorus hydrides should be responsible for the superconductivity observed at 200 GPa in Drozdov’s work. Since Drozdov et al. increased the pressure at low temperature ($T < 200$ K) [15], we speculate that this discrepancy is due to the different experimental protocols used in these two works. Low temperature could hinder the polymerization/decomposition of phosphorus hydrides and secure phosphorus hydrides to much higher pressure.

To find out whether low temperature can hinder the reactions and further identify the superconducting candidate, we studied the high-pressure behavior of PH₃ at low temperature (<200 K). First, we compressed PH₃ up to 31 GPa, when P₂H₄ dimerized into P₄H₆ at room temperature. However, after we decompressed the sample to ambient pressure at low temperature, the sample became transparent again (the inset image in Fig. 3a). As shown in Fig. 3a, the sample decomposed after laser irradiation and the resulting opaque solid (the inset image in Fig. 3a was identified as Hittorf’s phosphorus) and two characteristic Raman modes from P₂H₄ (2307 and 2317 cm⁻¹) were also found. The transparency of the residue and strong peaks from P₂H₄ suggest P₂H₄ was dominant in the sample decompressed from 31 GPa at low temperature. However, it can only survive below 25 GPa at room temperature, proving that low temperature can greatly hinder the polymerization of phosphorus hydrides. We further compressed the sample up to 60 GPa, and studied the Raman spectrum of the quenched residue. Similar photodecomposition and typical Hittorf’s P Raman modes (Supplementary Fig. 5, available as Supplementary Data at NSR...
(a) Phonon dispersions, phonon density of states projected onto atoms (PHDOS), the spectral functions \( \alpha^2 F(\omega)/\omega \) and electron–phonon coupling integration of \( \lambda(\omega) \) for the (a) Cmcm structure at 100 GPa and (b) C2/m structure at 200 GPa, respectively.

As shown in Fig. 3d, at room temperature, two-step dimerization occurred at around 12 and 25 GPa, and \( \text{P}_4\text{H}_6 \) finally decomposed into elemental phosphorus at 35 GPa. However, at low temperature, \( \text{P}_2\text{H}_4 \) could exist up to 60 GPa. \( \text{P}_4\text{H}_6 \) was maintained from 102 to 205 GPa.

### Theoretical calculations

We further performed structural searches on \( \text{P}_4\text{H}_6 \) at 100, 150 and 200 GPa with maximum simulation cells up to 4 formula units (f.u.); two stable structures with space group Cmcm (<182 GPa) and C2/m (>182 GPa) were found. Phonon dispersions calculations of the two structures do not give any imaginary frequencies and therefore this verifies their dynamic stabilities (Fig. 4). The superconducting \( T_c \) was estimated using the Allen and Dynes modified McMillan equation [34] with a typical choice of \( \mu^* = 0.13 \). The electron–phonon coupling constant \( \lambda \) of the Cmcm structure is only 0.59 (Table 1) at 100 GPa, and a superconducting \( T_c \) of 13 K was obtained. A relatively large \( \lambda \) value of 1.39 was found for the C2/m structure at 200 GPa, and the superconducting \( T_c \) was estimated to be 67 K. As summarized in Table 1, the estimated \( T_c \) agrees with the values measured by Drozdov et al., suggesting that \( \text{P}_4\text{H}_6 \) could be responsible for the superconductivity.

Similar to \( \text{H}_2\text{S} \), \( \text{PH}_3 \) is unstable at high pressure. Instead of becoming more hydrogen-enriching, it dehydrogenates through a series of polymerization/decomposition processes upon compression. This could be one of the critical factors that limit the maximum \( T_c \) near 100 K, at the same pressure where the H–S system has a \( T_c \) up to 180 K. These phenomena from \( \text{H}_2\text{S} \) and \( \text{PH}_3 \) highlight that avoiding the pressure-induced dehydrogenation or becoming more hydrogen-enriched is vital for a superconducting hydride with a high \( T_c \).

### CONCLUSION

In summary, we determined the stability of \( \text{PH}_3 \) under high pressure. At room temperature, two steps of polymerization were obtained. \( \text{P}_2\text{H}_4 \) and \( \text{P}_4\text{H}_6 \) were the reaction products of the first and second step.
dimerization, respectively. Above 35 GPa, the generated $P_4H_6$ completely decomposed into elemental phosphorus. However, at low temperature, $P_4H_6$ could remain up to 205 GPa. Vibrational measurements and theoretical simulation confirmed the formation of $P_4H_4$ and $P_2H_6$, which enriches the phase diagram of the P–H system under high pressure. Our work proves that the $P_4H_6$ phase can be generated under high pressure and suggests that it might be responsible for the reported superconducting transition.

**METHODS**

Solidified PH$_3$ was prepared via a cryogenic method and sealed into a symmetric DAC at $\sim$2 GPa for our *in situ* high-pressure measurements. T301 stainless steel and tungsten gaskets were used for the room-temperature and low-temperature measurements, respectively. The ruby fluorescence and Raman shifts of the diamond were used to investigate the pressure. A micro-Raman system (Renishaw, UK) with a 532-nm laser excitation was used to obtain the sample’s Raman spectra. The high-pressure *in situ* IR spectra were collected on a Bruker VERTEX 70v FTIR spectrometer and a custom-built IR microscope. High-pressure XRD measurements were carried out at the BL15U1 beamline of the Shanghai Synchrotron Radiation Facility ($\lambda = 0.6199$ Å) [35]. Low temperature was generated by cryostat using liquid nitrogen. Detailed information about each cycle is provided in the Supplementary Materials, available as Supplementary Data at NSR online. The *ab initio* structure predictions for $P_4H_6$ were performed using the particle swarm optimization technique implemented in the CALYPSO code [36,37]. CALYPSO has been used to investigate many materials at high pressures [38–42]. The *ab initio* structure relaxations were performed using density functional theory with the Perdew–Burke–Ernzerhof generalized gradient approximation implemented in the Vienna *ab initio* simulation package (VASP) [43]. Details of the simulations are provided in the Supplementary Materials, available as Supplementary Data at NSR online.

**SUPPLEMENTARY DATA**

Supplementary data are available at NSR online.

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