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Ternary superconducting cophosphorus hydrides stabilized via lithium

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Inspired by the diverse properties of sulfur hydrides and phosphorus hydrides, we combine first-principles calculations with structure prediction to search for stable structures of Li–P–H ternary compounds at high pressures with the aim of finding novel superconductors. It is found that phosphorus hydrides can be stabilized under pressure via additional doped lithium. Four stable stoichiometries LiPH_3 , LiPH_4 , LiPH_6 , and LiPH_7 are uncovered in the pressure range of 100–300 GPa. Notably, we find an atomic LiPH_6 with $Pm\bar{3}$ symmetry which is predicted to be a potential high-temperature superconductor with a T_c value of 150–167 K at 200 GPa and the T_c decreases upon compression. All the predicted stable ternary hydrides contain the P–H covalent frameworks with ionic lithium staying beside, but not for $Pm\bar{3}$ - LiPH_6 . We proposed a possible synthesis route for ternary lithium phosphorus hydrides: $\text{LiP} + \text{H}_2 \rightarrow \text{LiPH}_n$, which could provide helpful and clear guidance to further experimental studies. Our work may provide some advice on further investigations on ternary superconductive hydrides at high pressure.

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INTRODUCTION

Given the metallization and potential room temperature superconductivity of solid hydrogen under high pressure have been proposed,^{1,2} considerable efforts have been exerted in finding metallic hydrogen. Recently, solid hydrogen metallization has been reported to be realized at 495 GPa,³ but further evidence is needed. Although experimental observations of the metallic hydrogen phase remain controversial, researchers have agreed that hydrogen requires considerable high pressure to reach the metallic state. Doping hydrogen by an impurity has been considered a method for reducing the metallization pressure of pure hydrogen. Ashcroft⁴ suggested that the metallic hydrogen-rich compounds, such as Group IVa dense hydrides, can be metallic at lower pressures than those necessary for hydrogen given the “pre-compression” provided by non-hydrogen elements. Extensive theoretical investigations have explored that many hydrogen-rich compounds are potential superconductors with rather high superconducting transition temperature (T_c),^{5,6} such as H_3S with T_c of 204 K at 200 GPa,^{7,8} TeH_4 with T_c of 104 K at 170 GPa,⁹ Si_2H_6 with T_c of 139 K at 275 GPa,¹⁰ CaH_6 of 235 K at 150 GPa,¹¹ YH_{10} of 326 K at 250 GPa,^{12,13} LaH_{10} of 286 K at 210 GPa.^{12,13} Excitingly, hydrogen-rich superconductors H_3S ^{14,15} and LaH_{10} ^{16,17} have been successfully confirmed experimentally.

Motivated by the discovery of the high T_c superconductor H_3S under high pressure, Eremets et al.¹⁸ compressed PH_3 and found a T_c of 103 K at 207 GPa. However, the structural information and the origin of the high T_c phase were undetermined. Then, people have exerted efforts on determining this high T_c phase. Theoretical studies showed that all the predicted phosphorus hydrides PH_n ($n = 1–6$) at high pressure were thermodynamically metastable relative to elemental P and solid H_2 .^{19–21} Among these metastable phases, PH_2 possesses the lowest enthalpy with T_c of 76 K²¹ which responds to the superconducting phase in experimental work.¹⁸ Liu et al.²⁰ theoretically searched the structure of PH_3 under high pressure and found that the $C2/m$ phase with T_c of 83 K at 200 GPa is in line with the experimental report.²⁰

Experimentally, the PH_3 is found to be gradually decomposed into P_2H_4 , P_4H_6 , and then further into elemental phases above 35 GPa at room temperature.^{22,23} But at lower temperature, P_4H_6 can be stable up to 207 GPa.²³

Although phosphorus is adjacent to sulfur in the periodic table, and the predicted phosphorus hydrides have similar covalent bonds with those in sulfur hydrides, phosphorus hydrides are metastable, whereas sulfur hydrides prefer to form stable H_3S under high pressures. Considering that sulfur ($3s^23p^4$) has one more valence electron than phosphorus ($3s^23p^3$), phosphorus hydrides can be stabilized under pressure by introducing additional electrons. Therefore, we try to dope lithium into the P–H system, and expect to find the stable hydrogen-rich ternary compounds with potential high-temperature superconductivity.

At present, researches on binary hydrogen-rich superconducting compounds have been fruitful and matured, and ternary hydrogen-rich superconducting compounds have gradually been taken seriously. High-pressure experiments found that the ternary hydride BaReH_9 is a superconductor with T_c about 7 K at 100 GPa.²⁴ Also in theoretical work, the T_c of Fe_2SH_3 ,²⁵ YS_4H_4 ,²⁶ and YSH_5 ²⁷ at 173, 200, and 300 GPa is about 0.3, 20, and 0.7 K, respectively. Earlier, through theoretical calculations, our group found that after the introduction of Mg in the insulating CH_4 system, the T_c of MgCH_4 can reach 120 K at 121 GPa.²⁸ Recently, K was also doped into the CH_4 system in theoretical work²⁹ and T_c was predicted to be 12.7 K at 80 GPa. In addition, through adding Li into poor superconductive MgH_{12} , Sun et al.³⁰ found a high- T_c superconductor $\text{Li}_2\text{MgH}_{16}$ with T_c about 473 K at 250 GPa. What is more, theoretical calculations show that the introduction of alkali metal and alkaline earth metal elements can make the binary Au–H system stable under ambient pressure, and T_c of the $\text{Ba}(\text{AuH}_2)_2$ under ambient pressure is approximate to be 30 K.³¹

In fact, the precise exploration of the thermodynamic stability of the ternary stoichiometry system is a challenge. For the Li–P–H system, Li and P elements, Li–P, P–H, and Li–H binary boundary compounds are all systematically investigated and

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Fig. 1 The ternary phase diagram of Li, P, and H at **a** 100, **b** 200, and **c** 300 GPa. The corresponding elements and boundary binary phases are chosen from the results of the previous works.^{32,35,36,43,50,51} The dots represent compositions sampled in our preliminary predictions; dash lines show the synthetic route chosen for further binary convex hulls. Solid and hollow squares represent thermodynamically stable or metastable compositions on the ternary convex hull

Fig. 2 **a** The enthalpies of formation of LiPH_n ($n = 1-7$) with respect to LiP and H_2 at 100–300 GPa. **b** The phase transition series of stable compounds LiPH_3 , LiPH_4 , LiPH_6 , and LiPH_7

exhibit interesting superconducting properties under high pressure.^{18–23,32–36} Li–P compounds are well known as potential solid-state electrolytes in lithium-ion batteries and recently was discovered to be superconductive in Li_3P with T_c about 39.3 K under high pressure.³⁶ But LiP stoichiometry gets little attention owing to its poor Li content. At ambient condition, LiP is found to be stable and nonmetal with $P2_1/c$ symmetry.^{37,38} Under high pressure,^{35,36} LiP firstly decomposes into Li_3P and P above 13.5 GPa, then it becomes stable again with $P4/mmm$ symmetry above 60 GPa and retains stable till 300 GPa.

Here, we investigated the stabilities and structures of LiPH_n ($n = 1-7$) in the pressure range from 100 to 300 GPa through

synthetic route $\text{LiP} + \text{H}_2 \rightarrow \text{LiPH}_n$. Hydrogen-rich compositions, namely, LiPH_3 , LiPH_4 , LiPH_6 , and LiPH_7 , are found to be stable at high pressure. Above 250 GPa, LiPH_6 is thermodynamically stable with $Pm\bar{3}$ symmetry, which is isostructural with ternary hydrides MgSiH_6 and MgGeH_6 .^{39,40} $Pm\bar{3}$ - LiPH_6 is calculated to be a potential high- T_c superconductor with T_c about 150–167 K at 200 GPa and the T_c reduces with pressure increasing.

RESULTS AND DISCUSSION

We performed the full structure search of the Li–P–H ternary compounds at 100, 200, and 300 GPa by the ab initio evolutionary algorithm as implemented in the USPEX^{41,42} and constructed the ternary phase diagram in Fig. 1. It is shown that stoichiometries LiPH_6 and LiPH_7 locate on the convex hull at 100 and 200 GPa. Besides, we found two metastable compounds LiPH_3 and LiPH_4 which are only 9.9 and 2.0 meV/atom above the convex hull at 200 GPa. At 300 GPa, all ternary compounds become metastable, but LiPH_6 and LiPH_7 are only 9.1 and 7.0 meV/atom away from the convex hull, respectively. As expected, the LiPH_n compounds can be thermodynamically stable under high pressures. For judging the specific synthesis routes for ternary hydrides, our group proposed “triangle straight-line method” (TSLM).³¹ Through this method, if one ternary compound in the ternary convex hull lies on a straight line connected by any two stable species, then the ternary compound can be synthesized by the two species. In the convex hull of Li–P–H, we found that the stable compounds LiPH_6 and LiPH_7 lie on the connecting straight line between LiP binary compounds and H_2 . Herein, the synthetic route $\text{LiP} + \text{H}_2 \rightarrow \text{LiPH}_n$ we have chosen for the lithium phosphorus ternary hydrides can be considered feasibly.

Furthermore, we conducted the structure predictions of LiPH_n ($n = 1-7$) with simulation size ranging from two to four for each stoichiometry at the 100, 200, 250, and 300 GPa. The energetic stabilities of LiPH_n ($n = 1-7$) compounds are evaluated by their formation enthalpies compared with LiP and H_2 , as depicted in Fig. 2a. The stable structures of H_2 were taken from the work of Pickard et al.,⁴³ and LiP was taken from the work of Zhao et al.³⁶ As observed, compared with LiP and H_2 solids, the stoichiometries of LiPH_6 and LiPH_7 are stable and remain on the convex hull in the pressure range from 100 to 300 GPa; LiPH_3 and LiPH_4 emerge on the convex hull at 200 and 150 GPa and remain stable until 300 and 250 GPa, correspondingly. To further ensure the stabilities of ternary hydrides, we calculated the formation enthalpies of the above-mentioned LiPH_n compounds with respect to two other routes (see Supplementary Fig. 1): $\text{Li}_3\text{P} + \text{P} + \text{H}_2$ and $\text{LiH} + \text{P} + \text{H}_2$. With respect to Li_3P , P , and H_2 , all the predicted phases are stable in the whole pressure range. With respect to LiH , P , and H_2 , the

Fig. 3 The crystal structures of **a** $P2/m$ - LiPH_3 , **b** $P2_1/m$ - LiPH_4 , **c** $C2/c$ - LiPH_6 , **d** $Pm\bar{3}$ - LiPH_6 , **e** $P\bar{1}$ - LiPH_7 , and **f** $C2/m$ - LiPH_7 . Lithium atoms are colored green, phosphorus atoms are purple, and hydrogen atoms are pink

LiPH becomes unstable in the whole pressure range. Combining the data given in the convex hull (Fig. 2a), the final phase diagram of LiPH_n is demonstrated in Fig. 2b. The LiPH_3 is stable with $P2/m$ structure from 200 to 300 GPa, and LiPH_4 is stable with $P2_1/m$ structure from 150 to 250 GPa. LiPH_6 is stable with $C2/c$ structure from 100 to 250 GPa and then convert into the cubic $Pm\bar{3}$ structure. LiPH_7 started to be stable from 100 GPa with $P\bar{1}$ structure and transformed to $C2/m$ structure at 250 GPa.

Zero-point energy (ZPE) has been important in the total energy of hydrogen-rich compounds. Therefore, we used the quasi-harmonic model to estimate the ZPE of LiPH_n ($n=1-7$) compounds under 300 GPa (see Supplementary Fig. 2). After considering the ZPE, the formation enthalpies of the predicted phases at 300 GPa are not various obviously and the overall stability does not change. Thus, the ZPE does not considerably influence the total stability of the phase diagram. The phonon band structures of all thermodynamically stable phases are exhibited in Supplementary Fig. 3. The lack of imaginary phonon frequency indicates that they are all dynamically stable.

A survey of the distinctive features of the predicted structures is displayed in Fig. 3, and the structure parameters are listed in Supplementary Table 1. For $P2/m$ - LiPH_3 at 200 GPa, the P atoms formed distorted cubic units with the P–P bonds at approximately 2.10 Å. In the electron localization function (ELF) presented in Supplementary Fig. 4, electrons accumulate between P atoms, thereby indicating the P–P covalent bonds. The distorted cubic connected each other into a sheet with hydrogen saturating the dangling bonds. In the P–H sheets, every distorted cubic unit contains a monoatomic H at the center. Symmetrical with the P–H sheet, two other kinds of sheets are stacked along the b -axis: one consists of Li atoms; another consists of H_2 units with 0.88 Å bond lengths and monoatomic hydrogen atoms. For $P2_1/m$ - LiPH_4 at 150 GPa, high electron densities are found between P–P and P–H in the ELF. Therefore, P atoms connect as zigzag chains with P–P bonds at approximately 2.10 Å. Every P atom connects four H atoms with P–H bonds ranging from 1.40 to 1.44 Å. Li atoms arrange along the P–H chains. When hydrogen content increases, as indicated in the ELF, P atoms absorb additional hydrogen atoms and form PH_n units. In $C2/c$ - LiPH_6 and $P\bar{1}$ - LiPH_7 at 250 and 150 GPa, the PH_6 units are found as distorted octahedrons with P–H bonds at approximately 1.35–1.36 and 1.37–1.40 Å, correspondingly. In the high-pressure range, $C2/m$ - LiPH_7 possesses PH_{11} units with P–H bonds at approximately 1.50–1.58 Å at

300 GPa. Every PH_{11} unit is connected by H–H bonds with 0.96 and 1.07 Å. At above 250 GPa, the $C2/c$ phase of LiPH_6 transforms into an A15-like structure with $Pm\bar{3}$ symmetry, that is, isostructural with MgSiH_6 and MgGeH_6 predicted by our group.^{31,40} In $Pm\bar{3}$ - LiPH_6 , the H–H distances are 1.14 Å at 300 GPa and low electron densities between all the atoms in the ELF indicate the atomic character of this phase.

In previous theoretical works on the metastable P–H system, most PH_n ($n=1-3$) structures consist of P–P layers or P–P chains with H atoms hanging on the P frameworks by P–H bonds.^{19–21} The dimensionality of the P frameworks decreases from layers (PH , PH_2) to chains (PH_3 , PH_4). Then, in PH_5 and PH_6 , the P–H polymers exist and connected by H–H bonds.¹⁹ In LiPH_n ($n=1-7$), except for the atomic phase $Pm\bar{3}$ - LiPH_6 , the P–H and P–P sublattices in LiPH_n ($n=1-7$) structures are similar to those in the PH_n structures, that is, the layers of PH in LiPH_3 , the chains of PH_4 in LiPH_4 , and the polymers of PH_6 and PH_{11} in LiPH_6 and LiPH_7 . Thus, lithium does not change the connect manner of phosphorus and hydrogen but stabilize the phosphorus hydrides under high pressure.

Before calculating the superconductive properties of LiPH_n compounds, we explored their electronic structures. In the calculated band structures with projection (Fig. 4), except for the low-pressure phases $C2/m$ - LiPH_6 and $P\bar{1}$ - LiPH_7 , all the other stable phases are metallic. The bands near the Fermi level are mainly provided by H and P and rarely come from Li. The Bader charge analysis⁴⁴ (see Supplementary Table 6) shows that Li and P atoms play roles as electron donors and provide electrons to H atoms. For all the stable phases, Li constantly loses approximately 0.8e. This phenomenon indicates that, for every metastable PH_n , nearly one electron is required for their stabilization, and this requirement is satisfied by lithium. However, the electrons that P loses and the electrons that H gains are different from each stable phase. For non-metallic phase $C2/c$ - LiPH_6 and $P\bar{1}$ - LiPH_7 , and poor metallic phase $P2_1/m$ - LiPH_4 , every P atom loses approximately 2.88, 2.76, and 1.43e, and every H atom receives nearly 0.61, 0.51, and 0.56e, respectively. For other metallic phases $P2/m$ - LiPH_3 , $Pm\bar{3}$ - LiPH_6 , and $C2/m$ - LiPH_7 , every P atom loses 0.23, 1.28, and 1.23e and every H atom receives 0.33, 0.34, and 0.29e, correspondingly. In metallic phases, fewer electrons around H atoms than those in non-metallic and poor metallic phases are present, thereby indicating more free electrons in metallic phases. With the increase in the H contents in metallic phases, the H-derived electronic DOS gradually dominates at the Fermi level

Fig. 4 Electron band structures of **a** $P2/m\text{-LiPH}_3$ at 200 GPa, **b** $P2_1/m\text{-LiPH}_4$ at 150 GPa, **c** $C2/c\text{-LiPH}_6$ at 250 GPa, **d** $Pm\bar{3}\text{-LiPH}_6$ at 300 GPa, **e** $P\bar{1}\text{-LiPH}_7$ at 150 GPa, and **f** $C2/m\text{-LiPH}_7$ at 300 GPa. The Fermi level is set to zero and depicted as the red dash line. The red, blue, and green dots represent the contributions of H, P, and Li atoms to the electron bands

N_F (Fig. 5). For $P2/m\text{-LiPH}_3$, the values P-derived electronic DOS contribute most to the N_F . For $Pm\bar{3}\text{-LiPH}_6$ and $C2/m\text{-LiPH}_7$, the values of N_F are mainly contributed by electrons projected to the H atoms. Therefore, the hydrogen-rich LiPH_n compounds may produce promising superconductivities.

We investigated the superconductivities of the metallic LiPH_n compounds at different pressures by calculating the EPC parameter λ , the logarithmic average phonon frequency $\omega_{\log}$, and the superconductive critical temperature T_c (Table 1). For poor metallic phase $P2_1/m\text{-LiPH}_4$ at 150 GPa, the λ is 0.25, and $\omega_{\log}$ is 1222.8 K. The small values of λ and $\omega_{\log}$ cause the low T_c at approximately 0.05 K, which is close to 0. For $P2/m\text{-LiPH}_3$ and $C2/m\text{-LiPH}_7$, the EPC parameters of λ are 0.82 and 0.74, and the

calculated $\omega_{\log}$ values are 1131.5 and 1434.0 K at 200 and 300 GPa, respectively. Using the corrected Allen–Dynes-modified McMillan equation, their T_c values are 48.8–60.4 and 46.0–59.2 K with the Coulomb pseudopotential $\mu^* = 0.1\text{--}0.13$, correspondingly.

Although atomic phase $Pm\bar{3}\text{-LiPH}_6$ starts to be stable above 250 GPa, we found that it can be dynamically stable when decompressed to 200 GPa, and we calculated the superconducting critical temperature T_c of $Pm\bar{3}\text{-LiPH}_6$ as a function of pressure (Table 1). At 200, 250, and 300 GPa, the calculated values of T_c are 167.3, 148.3, and 128.6 K, respectively. The Eliashberg phonon spectral function $\alpha^2F(\omega)$ and projected phonon density of states (PHDOS) of $Pm\bar{3}\text{-LiPH}_6$ at different pressures are illustrated in Fig. 6. Under the pressures of 200, 250, and 300 GPa, the contributions

of Li, P, and H atoms to the total λ and total $\omega_{\log}$ are shown in Fig. 6. The P atoms dominate the low-frequency regions (0–500 cm^{-1}) which contribute about 23.0–31.7% to the total λ and 5.7–8.6% to the total $\omega_{\log}$. For the case of Li atoms, they dominate the middle-frequency regions (500–1000 cm^{-1}), contribute about 13.0–17.8% to the total λ , and 3.8–3.9% to the total $\omega_{\log}$. While the H atoms which dominate the high-frequency regions (>1000 cm^{-1}) contribute about 55.3–59.2% to the total λ and 87.5–90.4% to the total $\omega_{\log}$. Hydrogen plays a dominating role in electron–phonon coupling and logarithmic average phonon frequency. Therefore, the high T_c of $Pm\bar{3}$ -LiPH₆ mainly comes from H atoms.

With the increase in pressure, the T_c decreases from 167.7 to 128.6 K. At the same time, the $\omega_{\log}$ increases from 1119.2 to 1429.4 K whereas λ decreases from 1.62 to 1.11. Therefore, the change of T_c is dominated by λ under pressure. We further studied the change of the partial $\omega_{\log}$ and λ of Li, P, and H atoms under pressure (Table 2). From 200 to 300 GPa, the $\omega_{\log-P}$ reduces from 96.1 to 81.4 K while the $\omega_{\log-Li}$ increases from 43.8 to 55.6 K. As a result, the total value of low- and middle-frequency $\omega_{\log-LiP}$ are almost unchanged under pressure. The increase of $\omega_{\log}$ is mainly due to the increase of $\omega_{\log-H}$ (from 979.3 to 1292.4 K).

Fig. 5 Electron density of states of **a** $P2/m$ -LiPH₃ at 200 GPa, **b** $P2_1/m$ -LiPH₄ at 150 GPa, **c** $Pm\bar{3}$ -LiPH₆ at 300 GPa, and **d** $C2/m$ -LiPH₇ at 300 GPa. The Fermi level is set to zero and depicted as the red dash line. The black solid line represents the total density of states. The pink, purple, and green solid line represent the electron density of states projected onto H, P, and Li atoms, respectively

With the increase of pressure, the partial constants of EPC λ_H and λ_P reduce a lot from 0.895 to 0.675 and 0.515 to 0.256, respectively, while the λ_{Li} varies little from 0.210 to 0.197. Thus, the decrease of λ is mainly dominated by the reduction of λ_H and λ_P , which is due to the large contribution of H and P atoms to the Fermi level N_F .

The predicted metastable superconductor PH₃ possesses T_c at approximately 83 K with estimated λ and $\omega_{\log}$ at nearly 1.45 and 826 K for 200 GPa.²⁰ At the same pressure, $Pm\bar{3}$ -LiPH₆ has a T_c at approximately 149.6–167.3 K with λ and $\omega_{\log}$ at nearly 1.62 and 1119.2 K, respectively. The λ and $\omega_{\log}$ values of $Pm\bar{3}$ -LiPH₆ are larger than those of PH₃, thus causing a larger T_c . The doping of Li atom makes the total mass of LiPH₆ lighter than that of PH₃, which can produce a large Debye temperature. Moreover, three clear phonon frequency regions that correspond to P, Li, and H can be found in $Pm\bar{3}$ -LiPH₆ and the atomic H has a wide and continuous high-vibration frequency region (1000–2500 cm^{-1}) and contributes considerably to the EPC. In the case of PH₃, strong hybridization of P and H makes the low- and middle-frequency regions contribute most to the total EPC, thereby possibly causing a low λ value.

To further explore the superconductivities and provide some information to experiment, the McMillan isotopic coefficient β and critical magnetic fields $\mu_0 H_c(0)$ of LiPH_n ($n = 3, 6$, and 7) and critical temperature T_c of LiPD_n ($n = 3, 6$, and 7) are estimated in Table 1. Because the T_c of LiPH₄ is near zero, we did not calculate its β , $\mu_0 H_c(0)$, and T_c of LiPD₄. It is clear that the isotopic coefficient β values always maintain about 0.5. For $P2/m$ -LiPH₃ and $C2/m$ -LiPH₇, the critical magnetic fields $\mu_0 H_c(0)$ are estimated to be about 6.8–8.5 and 6.4–8.4 T at 200 and 300 GPa, respectively. For the high- T_c superconductor $Pm\bar{3}$ -LiPH₆, the estimated $\mu_0 H_c(0)$ value is as high as 28.7–32.9 T at 200 GPa, and gradually decreases to 16.1–19.0 T at 300 GPa.

In summary, we have explored the crystal structures and stabilities of Li–P–H ternary system under high pressure by employing the evolutionary algorithm USPEX in combination with first-principles calculations. It is found that Li can stabilize metastable P–H compounds and form stable ternary hydrides LiPH₃, LiPH₄, LiPH₆, and LiPH₇ under high pressure. Except for the low-pressure phases of $C2/c$ -LiPH₆ and $P\bar{1}$ -LiPH₇, all the other stable LiPH_n phases are metallic. Among the metallic phases, $P2/m$ -LiPH₃ and $C2/m$ -LiPH₇ are superconductive with T_c of 49–60 and 46–59 K at 200 and 300 GPa, respectively. Their critical magnetic fields are about 6–8 T. Significantly, atomic phase $Pm\bar{3}$ -LiPH₆ has a high T_c and high $\mu_0 H_c(0)$ values about

Table 1. The calculated EPC parameter (λ), logarithmic average phonon frequency ($\omega_{\log}$), critical temperature with $\mu^* = 0.10$ and 0.13 (T_c and $f_1 f_2 T_c$), electron density of states at the Fermi level (N_F , states/spin/Ry/Unit Cell), McMillan isotopic coefficient (β), and critical magnetic fields ($\mu_0 H_c(0)$) with $\mu^* = 0.10$ and 0.13, and Somerfield constant (γ) for LiPH_n compounds at given pressures

Parameter	$P2/m$ -LiPH ₃	$P2_1/m$ -LiPH ₄	$Pm\bar{3}$ -LiPH ₆			$C2/m$ -LiPH ₇
	200 GPa	150 GPa	200 GPa	250 GPa	300 GPa	300 GPa
λ	0.82	0.25	1.62	1.29	1.11	0.74
$\omega_{\log}$ (K)	1131.5	1222.8	1119.2	1311.4	1429.4	1434.0
N_F	4.72	2.19	4.72	4.33	4.02	5.08
T_c (K)	45.9–56.3	0.00–0.05	125.3–136.5	114.2–127.5	100.1–115.3	43.8–55.9
$f_1 f_2 T_c$ (K)	48.8–60.4	0.00–0.05	149.6–167.3	128.7–148.3	110.9–128.6	46.0–59.2
β	0.44–0.47	–	0.48–0.49	0.47–0.48	0.46–0.48	0.46–0.43
γ	2.98	–	4.29	3.44	2.94	3.07
$\mu_0 H_c(0)$ (T)	6.8–8.5	–	28.7–32.9	20.9–24.4	16.1–19.0	6.4–8.4
$f_1 f_2 T_{c-LiPDn}$ (K)	38.2–47.3	–	116.4–129.5	100.4–113.9	86.9–100.5	35.7–45.9

The calculated critical temperature ($f_1 f_2 T_{c-LiPDn}$) with $\mu^* = 0.10$ and 0.13 of LiPD_n ($n = 3, 6$, and 7) compounds at given pressures

Fig. 6 The phonon band structure (left), PHDOS, and Eliashberg spectral function $\alpha^2 F(\omega)$ (right) for $Pm\bar{3}$ -LiPH₆ at different pressures. Red solid circles indicate the phonon line width with a radius proportional to the EPC strength. The integral λ and $\omega_{\log}$ as a function of frequency are calculated and shown in red and blue solid lines. The contributions of the P, Li, and H atoms are illustrated in percentages

Table 2. The partial and total constants of the electron–phonon interaction λ , partial and total logarithmic average phonon frequencies $\omega_{\log}$, and the partial and total root-mean-square frequencies ω_2 of $Pm\bar{3}$ -LiPH₆ at 200, 250, and 300 GPa

	200 GPa	250 GPa	300 GPa
λ_H	0.895	0.751	0.657
λ_{Li}	0.210	0.201	0.197
λ_P	0.515	0.338	0.256
λ	1.62	1.29	1.11
$\omega_{\log-H}$ (K)	979.3	1174.8	1292.4
$\omega_{\log-Li}$ (K)	43.8	49.8	55.6
$\omega_{\log-P}$ (K)	96.1	86.8	81.4
$\omega_{\log}$	1119.2	1311.4	1429.4
ω_{2-H} (K)	1269.8	1454.2	1588.7
ω_{2-Li} (K)	143.2	184.4	218.3
ω_{2-P} (K)	267.1	257.1	245.7
ω_2	1680.1	1895.7	2052.7

149–167 K and 28.7–32.9 T at 200 GPa, respectively. As pressure increases to 300 GPa, the T_c and $\mu_0 H_c(0)$ decrease to 110–128 K and 16.1–19.0 T, correspondingly. The high T_c value of $Pm\bar{3}$ -LiPH₆ under pressure is closely related to the large H-derived electronic DOSs at the Fermi level, strong EPC and high logarithmic average frequency associated with vibrations of atomic H, and the light masses of Li atoms. The exploration of ternary phase diagrams is a challenging task, but the study of ternary hydrides remains valuable. Ternary hydrides frequently achieve some goals that are unachievable in binary hydrides by introducing a third type of element, such as stabilizing the metastable binary hydrides, metalizing the insulative binary hydrides with strong covalent bonds, further reducing the superconducting pressures of some high T_c binary hydrides. Furthermore, ternary hydrides may produce some other new high T_c phases, such as the atomic phase of $Pm\bar{3}$ -LiPH₆.

METHODS

Variable composition searches of the Li–P–H ternary phase at 100, 200, and 300 GPa were conducted through the evolutionary algorithm USPEX^{41,42} code with respect to element Li, P, and H. One hundred and twenty structures were created using a random symmetric generator in the first generation, all subsequent generations contained 85 structures and were produced using variation operators such as heredity (50%), softmutation (20%), transmutation (10%), 20% of each new generation was produced randomly. Then, we explored the stable compounds of LiPH_n ($n = 1–7$) based on the fixed composition search implemented by USPEX^{41,42} with respect to the binary compounds LiP and H₂. It was performed at 100, 200, 250, and 300 GPa using original cells ranging from two to four formula units. All the structural relaxations, electronic properties, and total energy calculations are conducted using the VASP package⁴⁵ in the framework of DFT with Perdew–Burke–Ernzerhof parameterization of the generalized gradient approximation.⁴⁶ The projector-augmented wave approach⁴⁷ was adopted to describe ion–electron interactions, where $1s^1$, $1s^2 2s^1$, and $3s^2 3p^3$ are considered as valence electrons for H, Li, and P atoms, respectively. A plane-wave energy cutoff of 800 eV was used. We applied a Brillouin zone sampling grid spacing of $2\pi \times 0.03 \text{ \AA}^{-1}$ for structure relaxations and $2\pi \times 0.02 \text{ \AA}^{-1}$ for electronic property calculations. Lattice dynamics and electron–phonon coupling (EPC) were characterized by density functional perturbation theory as implemented in the Quantum-ESPRESSO package.⁴⁸ Norm-conserving potentials for H ($1s^1$), Li ($1s^2 2s^1$), and P ($3s^2 3p^3$) were used with a kinetic energy cutoff of 80 Ry. The k - and q -points meshes in the first BZ are $24 \times 12 \times 24$ and $4 \times 2 \times 4$ for $P2_1/m$ -LiPH₃, $20 \times 20 \times 12$ and $5 \times 5 \times 3$ for $P2_1/m$ -LiPH₄, $24 \times 24 \times 24$ and $6 \times 6 \times 6$ for $Pm\bar{3}$ -LiPH₆, and $20 \times 20 \times 12$ and $5 \times 5 \times 3$ for $C2/c$ -LiPH₇. Their superconductive transition temperatures T_c are estimated through the

Allen–Dynes-modified McMillan equation with correction factors.⁴⁹ The calculation details of superconductive properties can be seen in Supplementary Information.

DATA AVAILABILITY

The datasets used in this article are available from the corresponding author upon request.

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AUTHOR CONTRIBUTIONS

T.C. and D.D. designed this projected. Z.S. performed the calculations. D.D. and Z.S. made the analysis and wrote the manuscript. All authors discussed the results and commented on the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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