Quasi-two-dimensional metallic hydrogen inside di-phosphide at high pressure

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Abstract. The method of mathematical modelling was used for the calculation of the structural, electronic, phononic, and other characteristics of various normal phases of phosphorus hydrides with stoichiometry $\text{PH}_k$. It was shown that the di-phosphine may form 2D lattice of the metallic hydrogen in it, stabilized by phosphorus atoms under high hydrostatic pressure. The resulting structure with the elements of H-P-H has a locally stable (or metastable) phonon spectrum. The properties of di-phosphine were compared with the properties of similar structures such as the sulphur hydrides.

1. Introduction
One of the search areas for the new superconducting materials with high critical temperatures is the study of compounds with high hydrogen content. In [1] it was discovered, that the transition to the superconducting state of the metallic phase of the hydrogen sulfide under pressure 170 GPa takes place at the temperature $T = 203$ K. The idea of the experiment was based on the theoretical works on the study of the metallic hydrogen properties, in which high critical temperature $T_c \sim 200 \div 400$ K [2] were predicted. In the works [3, 4] it was shown that such a hydrogen phase may be metastable. After publication of the results [1] the interest in searching for compounds that have higher $T_c$ temperatures has increased significantly. In particular, the preliminary experimental results on the compression of phosphide $\text{PH}_3$ and the effect of its superconductivity at 100 K [5] should be mentioned. The following fact was taken into account in [1]. At the higher pressure values the hydrogen forms a hydride $\text{SH}_n$ ($n \leq 3$) [6] through dissociation of the sulfur compounds. The specific properties of the $\text{SH}_3$ can lead to the possible explanation of the high-temperature superconductivity existence. In [7-9] the $\text{SH}_2$ phase with the symmetry $I4/\overline{1}mm$ was found along with the study of the properties of the $\text{SH}_3$ compound, for which the electron and phonon spectra and the density of electron and phonon states in the pressure range $100 \div 225$ GPa were calculated.

In this paper we present the calculations of the electronic and phonon properties of the di-phosphine $\text{H}_2\text{P}-\text{PH}_2$ system compressed with up to the 250 GPa hydrostatic pressures. Di-phosphine under normal conditions is a colorless liquid with the structure of molecules presented in Figure 1a [10].

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2. Method
The calculations of the structural, electronic and phonon characteristics of the molecules and the periodic crystal structure of PH$_k$ in the pressure range 0 ÷ 250 GPa were performed using ab-initio method. The DFT approximation with the plane wave basis with the correlation functional GGA – PBE pseudopotential which preserves the norm was used. The unit cell of the structure used to calculate the electronic properties contains an element such as H2P-PH2. All the calculations were performed in the spin-polarized approximation in order to compare the calculated energy values of different phases in an adequate manner.

3. Results
At the 25 GPa pressure the molecular di-phosphine P2H4 phase becomes metallic because of overlap of electron shells of the molecules. The compression of the combination of such molecules in the pressure range 25 ÷ 250 GPa leads to the formation of metallic crystalline phase. The main structural element of this phase H2P-PH2 acquires straight H-P-H bond directed at an angle of 180° (Fig. 1c). In calculations of the first cycle it was assumed that the pressure applying leads to the symmetry P1 of the initial cell containing the P$_2$H$_4$ molecule. The resulting crystal structure at the pressure of 25 ÷ 125 GPa acquires the I4/MMM symmetry of the unit cell. The structure formed in this pressure range with a final I4/MMM crystal symmetry (Fig. 1e) results from the structural modification of the unit cell in the studied phase with the stoichiometry P$_2$H$_4$. At the next stage of the calculations the cell with the symmetry I4/MMM was used as a starting one (second cycle). Crystal structure with this unit cell symmetry was studied in the pressure range 25 ÷ 250 GPa. In the entire pressure range 25÷250 GPa the structural modification of the P$_2$H$_4$ unit cell with the symmetry I4/MMM leads to formation of set of parallel planes containing either phosphorus or hydrogen atoms (Fig. 1e). The hydrogen atoms form a square lattice with a period depending on the pressure. As a result, the electronic properties of the system acquire quasi-two-dimensional character. The phosphorus atoms form their own planes. The first coordination sphere of phosphorus atoms consists of four P atoms located in above mentioned plane and two pairs of hydrogen atoms located above below it. At the pressure $P = 125$ GPa the calculated unit cell volume amounts to $V = 13.54$ Å$^3$, which gives the total electron density value $n = 10^{24}$ cm$^{-3}$ (14 electrons per cell, or about 1 elect./Å$^3$). The observed effect of the redistribution of the electron density between atoms with increasing pressure, determined by the conditional Mulliken charges of phosphorus $Z_M$(P) and hydrogen $Z_M$(H), should be considered as an interesting one. The Mulliken charge is positive for phosphorus and negative for hydrogen, its magnitude increases with pressure increase.

Figure 1. a – structure of di-phosphine under normal conditions; b – isosurface of the electron density for molecules of di-phosphine at the level of 0.6, indicating the covalent bonding in the molecule; c– a primitive cell with two elements of H-P-H at the pressure $P = 150$ GPa; d – the Brillouin zone corresponding to the primitive cell at the pressure $P = 150$ GPa; e – the structure formed from molecules of di-phosphine at the pressure $P = 150$ GPa; the two-dimensional distribution of electron density in the plane containing the hydrogen atoms is shown.
As follows from the results of the calculations presented here, the pressure \(P\) “pushes” the electron density away from the phosphorus atoms to the hydrogen ones. This effect can be interpreted as an actual "doping" of the hydrogen planes with the additional electrons. The results show a reduction of the distance between two hydrogen planes with pressure increase. The hydrogen atoms form a quasi-two-dimensional square lattice as result of this redistribution. The maximal concentration of hydrogen atoms within the planes occurs at the pressure \(P = 150\) GPa.

**Figure 2.** \(a\) – band structure of \(\text{P}2\text{H}4\) electrons at the pressure \(P = 175\) GPA; \(b\) – the partial density of of the states number: 1 – for \(s\)-electrons, 2 – for \(p\)-electrons, 3 – the total DOS.

**Figure 3.** \(a\) – phonon dispersion curves \(\text{P}2\text{H}4\) at the pressure \(P = 175\) GPA; \(b\) – PhDOS – phonon \(\text{P}2\text{H}4\) density of states, the maximum energy of the phonons at 175 GPA – \(h\nu \approx 270\) meV.

**Figure 4.** Change of the enthalpy \(\Delta H\) with pressure increase for different phases: 1– (\(\Delta\ ▲\)) – sulphide \(\text{SH}_2\) (symmetry \(I4/\text{MMM}\)); 2 – (\(\square\ ■\)) – di-phosphine \(\text{P}_4\text{H}_4\) (symmetry \(I4/\text{MMM}\)); 3 – (\(\circ\ ●\)) – \(\text{SH}_3\) (symmetry \(\text{IM}-3\text{M}\)); 4 – (\(\circ\ ●\)) – \(\text{PH}_3\) (symmetry \(\text{IMMM}\)). Open (\(\Delta, ■, ○, ◊\)) and closed (\(▲, ■, ●, ♦\)) symbols correspond to presence or absence of imaginary frequencies. 1a, 2a, 3a and 4a are the pressure intervals, in which the structures have only real frequencies.

The Figure 2 shows the properties of the electron subsystem for the pressure \(P = 175\) GPA. As seen, the Fermi level is located at the electronic DOS peak position and at least one of the zones has “dropped” below the Fermi level at this pressure. The estimation of effective masses of carriers gives
near the Fermi level a value of about 0.1 meV. At the pressure \( P = 175 \text{ GPa} \) the Fermi level crosses three subzones (Fig. 2).

There are no imaginary frequencies in the pressure range 50 \( \div \) 250 GPa in the phonon spectrum of the crystal \( \text{P}_2\text{H}_4 \rightarrow I4/\text{MMM} \) phase (Fig. 3). Therefore the phase \( \text{P}_2\text{H}_4 \rightarrow I4/\text{MMM} \) is stable in this pressure range. Maximum frequencies lie in the energy region of the order of 265 meV. Note that the optical modes corresponding to oscillation of hydrogen atoms (Fig. 3) exist at both at small \( q \) (point \( G \)) and segments connecting the symmetry points of the Brillouin zone (Fig. 1c). The phonon spectrum becomes more rigid with increasing pressure.

Pressure dependence of the enthalpy \( \Delta H \) is presented in Figure 4 for the most stable crystalline phases: \( \text{SH}_2 \) and \( \text{SH}_3 \) sulfide, di-phosphide \( \text{P}_2\text{H}_4 \) and phosphine \( \text{PH}_3 \). As follows from the Figure, the \( \text{XH}_2 \) compounds should be metastable, since their enthalpy is more than that for \( \text{XH}_3 \) phase. Laser-heating of \( \text{SH}_2 \) compressed in the diamond cell was used in experiments [1] to stimulate the \( \text{XH}_2 \) to \( \text{XH}_3 \) phase transition. The metastable \( \text{XH}_2 \) phase with the \( I4/\text{MMM} \) symmetry can be formed under compression of di-phosphine \( \text{P}_2\text{H}_4 \) without heating since in the range 50 \( \div \) 250 GPa its spectrum does not contain imaginary frequencies. In addition, for the phase having the \( \text{PH}_3 \) stoichiometry and the \( I\text{MM}M \) symmetry we obtained relatively small range of the pressure (100 \( \div \) 150 GPa) , in which imaginary frequencies are absent.

4. Conclusions

The \( \text{P}_2\text{H}_4 \) di-phosphine molecular phase becomes metallic at pressures more than 25 GPa because of overlap of the electron shells of molecules. In the range of pressure 50 \( \div \) 250 GPa the structural modification of the \( \text{P}_2\text{H}_4 \) unit cell causes formation of the \( I4/\text{MMM} \) symmetry (Fig. 1e). As a result, parallel planes of \( \text{P} \) and \( \text{H} \) atoms are formed and a square lattice is observed in hydrogen planes. The electronic properties of the system acquire quasi-two-dimensional metallic character. There are no imaginary frequencies in the phonon spectrum of the di-phosphine \( \text{P}_2\text{H}_4 \rightarrow I4/\text{MMM} \) crystal phase in the pressure range 50 \( \div \) 250 GPa, so it is stable (or metastable) this pressure range. The maximal frequency lies in the 265 meV energy region. In the narrow pressure range 100 \( \div \) 150 GPa the competing \( \text{PH}_3 \) phosphine phase has lowest enthalpy.

Hydrostatic pressure forms the hydrogen and phosphorus (or sulfur) planes and “pushes away” the electron density from the many-electron atoms (P or S) in hydrogen planes. Conventionally, this effect can be described as a “doping” of the planes.

Basing on the calculations we conclude that the optimal pressure for superconductivity in di-phosphine is about 150 GPa and suppose that its critical temperature is more than \( T_c \) for \( \text{PH}_3 \) [5] because in a wide range of pressures it has the properties of two-dimensional metallic hydrogen.

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