

## Two-dimensional metal-phosphorus monohydrides



Leonidas Tsetseris

Department of Physics, National Technical University of Athens, GR-15780 Athens, Greece

### ARTICLE INFO

#### Article history:

#### Keywords:

*ab initio*  
Topochemical  
Silicane  
Transistor  
Dirac point

### ABSTRACT

In the rapidly expanding field of two-dimensional (2D) materials, special attention is given to systems that can be stabilized as free-standing monolayers. Here we use density-functional theory calculations to show how a well-established synthesis route can prepare stable 2D sheets of P-based hydrides. In particular, we show that strongly exothermic topotactic reactions of suitable  $AlB_2$ -like precursors produce 2D materials with stoichiometries CuPH, AuPH, AgPH and PdPH. This novel family of monolayer systems provides multifunctional building blocks for devices as it includes metals, semimetals (with Dirac-like cones) and semiconductors with small or wide energy band gaps.

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### Introduction

Research on two-dimensional (2D) materials has already established several systems with high potential for employment in devices of different fields, such as electronics, optoelectronics, spintronics, catalysis, energy conversion and others [1–7]. In addition to graphene [8–11], transition metal dichalcogenides [1,12], derivatives of graphene and graphene-like materials [13–19], carbonitrides [5,20,21] and ultrathin oxides [22] are representative examples of 2D structures with intriguing properties and enhanced functionalities for a range of applications. By the same token, the quest to enlarge this family of materials becomes ever stronger, seeking to either add new derivatives of existing 2D systems, or identify configurations with unconventional stoichiometries [23–26].

One of the key challenges in current efforts is to obtain 2D materials that can exist as effectively free-standing sheets without covalent bonds to substrates. Moreover, it is often desirable to use a chemical approach to produce a large number of 2D sheets, and not just one or a few deposited monolayers. In this respect, one of the most promising synthesis routes is through so-called topotactic transitions [16,27–32] which produce silicane and germanane sheets (i.e., hydrogenated silicene or germanene) from  $CaSi_2$  and  $CaGe_2$  three-dimensional (3D) crystals with the well-known layered  $AlB_2$ -like structure [33–35]. Specifically, when  $CaSi_2$  or  $CaGe_2$  samples react with HCl acid [16,27–32], Ca atoms are de-intercalated and H atoms (or OH groups [30] in the case of siloxene) are attached to the silicene or germanene honeycomb

layers. In this way, stable silicane and germanane sheets are formed.

The main motivation for the present study is that, while many other  $AlB_2$ -like structures with less common compositions have been prepared experimentally [36–44], they have been completely overlooked, to the best of our knowledge, as precursors for the formation of 2D materials. In a recent study [33] we proposed with first-principles calculations that de-intercalation reactions can create 2D materials with composition AuGeH and  $AuGe_3H_3$ . In this work we also show that topotactic transformations of certain 3D structures could produce novel 2D materials with stoichiometries AuPH, CuPH, AgPH, and PdPH. The electronic profiles of these systems are remarkably diverse with metallic, semi-metallic and semiconducting behavior.

### Method

The results were obtained with Density Functional Theory (DFT) calculations using the plane wave-based code Quantum Espresso [45]. We employed Martins–Troullier (MT) pseudopotentials [46] or projected-augmented waves [47] (PAW) to describe the interactions between valence electrons and ions. Exchange and correlation effects among valence electrons were described with the PBE [48] or the PW91 [49] generalized-gradient approximation (GGA) functionals. Unless stated otherwise, the results we present below are based on MT-PBE calculations. The energy cutoff for the plane wave basis was varied up to 150 Rydbergs and fine  $k$ -point meshes (up to  $12 \times 12$ ) were used to ensure the convergence of energies and structural details.

The relaxation of atomic positions and lattice parameters was terminated when the energy converged within  $10^{-6}$  Ry. Since peri-

E-mail address: [leont@mail.ntua.gr](mailto:leont@mail.ntua.gr)

odic boundary conditions were enforced, a vacuum space at least 10 Å thick was placed between successive layers to make the artificial interactions among them negligible. Sampling of reciprocal space employed the Mohnkhorst–Pack scheme [50] of special  $k$ -points. Similar methodology has been applied in previous works on the properties of various materials [51–53].

## Results and discussion

The aluminum diboride ( $\text{AlB}_2$ ) structure is among the most common crystal geometries with whole families of materials adopting this form. The best-known class of  $\text{AlB}_2$ -like systems are the metal diborides with stoichiometry  $\text{MB}_2$  (M here is a metal atom) [34]. A crystal of the  $\text{AlB}_2$  type comprises planar honeycomb sheets of boron (in diborides) and intercalated metal atoms. The latter are located above (or below) the centers of the honeycomb hexagons. In addition to diborides, many more compounds crystallize in similar configurations with honeycomb sheets which are either planar or show various levels of corrugation [33,35]. Examples are the above-mentioned  $\text{CaSi}_2$  and  $\text{CaGe}_2$  precursors for the formation of silicane, siloxene, or germanane [16,18,19,27–32].

For the purposes of the present study, we probed the stability and structural features of the  $\text{AlB}_2$ -like crystals with composition  $\text{CaAuP}$ ,  $\text{CaCuP}$ ,  $\text{SrAgP}$ , and  $\text{SrPdP}$  [36–38]. Fig. 1 shows the arrangement of atoms in the  $\text{CaCuP}$  case. Here, Ca atoms are found between planar sheets which are akin to BN but made of Cu and P atoms. At least two basic  $\text{CaCuP}$  crystal polymorphs exist [35], depending on the relative position of Cu and P species between neighboring CuP layers. For example, Cu (or P) atoms may lie directly above and below Cu (or P) atoms of proximal sheets. Alternatively, the positions of Cu and P atoms may be interchanged when we move from one layer to the next one (as is true for the structure depicted in Fig. 1). Let us call these polytypes P2 and P1, respectively. Then, according to our DFT results, the most stable crystal structures for  $\text{CaCuP}$ ,  $\text{CaAuP}$ , and  $\text{SrAgP}$  ( $\text{SrPdP}$ ) are of the P1 (P2) type.

In analogy to  $\text{CaSi}_2$  and  $\text{CaGe}_2$ , if  $\text{CaCuP}$  reacts with HCl molecules, then Ca atoms can be removed to a crystalline  $\text{CaCl}_2$  phase [54]. In the process, H atoms can be attached to the CuP sheet and  $\text{H}_2$  molecules may be emitted. Formally, the reaction is described as

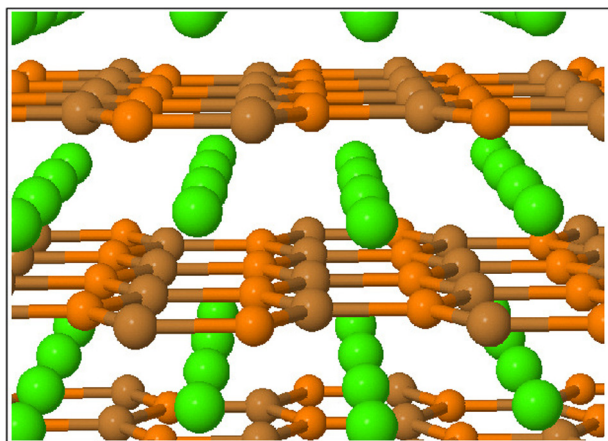
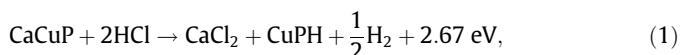
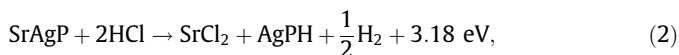


Fig. 1. The most stable polymorph of the  $\text{AlB}_2$ -like layered crystal of  $\text{CaCuP}$  (Ca: green, Cu: brown, P: orange spheres).

where the large value of 2.67 eV confirms its strong exothermic character. A similar topotactic reaction can transform  $\text{CaAuP}$  to 2D-AuPH with an energy gain of 2.76 eV. In the case of Sr-based precursors, the reaction creates the  $\text{SrCl}_2$  structure [55]. For example, in the case of  $\text{SrAgP}$  we have



while 3.05 eV of energy are released in the topotactic transformation of  $\text{SrPdP}$ .

Which are the structures attained by the product 2D-materials in the above reactions? To answer this question, we have probed the relative stability of several plausible configurations of metal–P hydride sheets. All these structures (named S1–S7) are shown, respectively, in Figs. 1–7 of the [Supplementary Material \(SM\)](#). Geometry S1 is obtained through structure relaxation starting from a CuP honeycomb lattice with hydrogen atoms attached to every phosphorus site. All configurations with H atoms attached to metal atoms have significantly higher energies. Likewise, isolated hydrogen vacancies have positive formation energies for the most stable structures reported in the following. Geometries S2 and S3 are obtained from the S1 configuration by doubling the unit cell along the direction of Cu–Cu bonds. In fact, the S1 polymorph of 2D-CuPH is dynamically unstable as it has imaginary frequencies in its phonon band structure. This is true also for the S1 configurations of 2D-AuPH and 2D-AgPH. On the other hand, we have checked that all the lowest-energy structures we report below are dynamically stable.

Fig. 2 shows top and side views of the most stable configuration of a CuPH sheet. It is an S5 polymorph with P–H bonds (their length is equal to 1.42 Å) pointing in either direction away from a flat Cu backbone. The structure is tetragonal with a lattice parameter of 3.90 Å. Each P atom occupies the apex of a square pyramid with Cu atoms at the base. The corresponding P–Cu bonds have a length of 2.32 Å and the unit cell contains two P atoms located above and below the Cu plane. Fig. 3 presents the energy band structure of

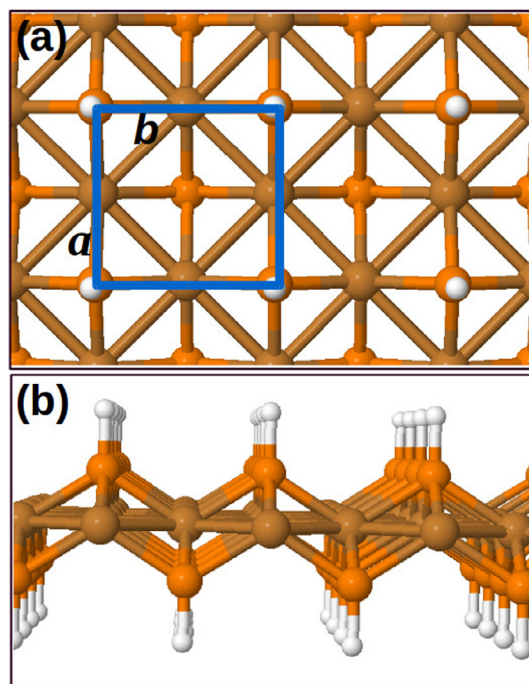


Fig. 2. (a) Top, and (b) side view of the lowest-energy CuPH monolayer structure (Cu: brown, P: orange, H: white spheres). The blue square shows the unit cell;  $a$  and  $b$  are the lattice parameters (here  $b$  is equal to  $a$ ).

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