Novel electronic properties of monoclinic MP$_4$ (M = Cr, Mo, W) compounds with or without topological nodal line

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Transition metal phosphides hold novel metallic, semimetallic, and semiconducting behaviors. Here we report by ab initio calculations a systematical study on the structural and electronic properties of MP$_4$ (M = Cr, Mo, W) phosphides in monoclinic $C2/c$ (C$\text{\textit{2}}$/c) symmetry. Their dynamical stabilities have been confirmed by phonon modes calculations. Detailed analysis of the electronic band structures and density of states reveal that CrP$_4$ is a semiconductor with an indirect band gap of 0.47 eV in association with the $p$ orbital of P atoms, while MoP$_4$ is a Dirac semimetal with an isolated nodal point at the $\Gamma$ point and WP$_4$ is a topological nodal line semimetal with a closed nodal ring inside the first Brillouin zone relative to the $d$ orbital of Mo and W atoms, respectively. Comparison of the phosphides with group VB, VIB and VIIB transition metals shows a trend of change from metallic to semiconducting behavior from VB-MP$_4$ to VIIB-MP$_4$ compounds. These results provide a systematical understanding on the distinct electronic properties of these compounds.

Transition metal phosphides (TMPs) have been attracted considerable research interest due to their structural and compositional diversity that results in a broad range of novel electronic, magnetic and catalytic properties\textsuperscript{1-4}. This family consists of large number of materials, having distinct crystallographic structures and morphologies because of choices of different TMs and phosphorus atoms\textsuperscript{5}. These compounds have been studied extensively due to their outstanding physical and chemical properties such as high catalytic activity\textsuperscript{6}, good electrical conductivity\textsuperscript{7}, and magnetocaloric behaviors\textsuperscript{8,9}. TMPs have been appeared as an efficient catalyst for hydrogen evolution reduction (HER)\textsuperscript{10}. For example, nanowires of FeP and FeP$_2$ have been used widely for hydrogen evolution in both strong alkaline and acidic aqueous solutions\textsuperscript{10}. CoP\textsuperscript{11}, CoP$_3$\textsuperscript{12}, and MoP$_2$\textsuperscript{13} are also reported as an excellent materials for HER and oxygen evolution reduction (OER), and have better stability because of the presence of a large number of negatively charge P-atom centers\textsuperscript{14,15}. In addition to electrocatalysis process, TMPs have various potential device applications, such as usage in electrotonic components, luminescent and semiconductor devices and as an anode material in lithium-ion batteries\textsuperscript{16-19}. Moreover, some TMPs such as TaP\textsuperscript{20} hold topological Weyl semimetal feature, and WP has been recently reported to have Dirac like points near the Fermi level\textsuperscript{21}. Similarly, transition metal diphosphide compounds, like MoP$_2$ and WP$_2$, were predicted as type-II Weyl topological semimetals\textsuperscript{22}.

Topological semimetals are not only of fundamental physical interests but also of great potential for future applications in quantum computation and spintronics\textsuperscript{23-28}. In topological semimetals, topological non-trivial band crossing points or line (line of nodes) exist in three-dimensional (3D) Brillouin zone (BZ) protected by certain symmetries\textsuperscript{29,30}. It can be classified into Dirac semimetal\textsuperscript{31}, Weyl semimeta\textsuperscript{32,33} and nodal line semimetal (NLSM)\textsuperscript{30,34-37}. Dirac semimetals have been theoretically predicted and experimentally confirmed in several materials such as Cd$_3$As$_2$\textsuperscript{31} and Na$_3$Bi\textsuperscript{32}. Topological Weyl semimetals have paring two-fold degenerate Weyl...
points with opposite distinct chiralities that may be right handed or left handed and have been realized in the materials breaking the time reversal ($T$) symmetry such as pyrochlore iridate\(^3\) or spatial inversion ($P$) symmetry such as TaAs family of compounds\(^8\). In NLSMs, the bands crossing points form continuous line rather than discrete points, generally enforced due to the band inversion mechanism\(^8,9\) and protected by $PT$ symmetry\(^3\). Topological NLSMs have been found in CaP\(^4\), Ca\(_3\)P\(_2\)\(^4\) phosphides and 3D graphene network structures\(^4\)–\(^5\), etc.

In this paper, based on ab initio calculations, we systematically investigate the transition metal phosphides $MP_4$ ($M = Cr, Mo, W$) for the structural stability and electronic properties. These three compounds are all in monoclinic phase with $C2/c$ ($C_{6h}^2$, No. 15) symmetry, while $CrP_4$ and $MoP_4$ have been experimentally synthesized\(^5\) and $WP_4$ is not yet reported. Their mechanical stabilities are confirmed with phonon mode analysis. Electronic band calculations show that $CrP_4$ is a semiconductor with an indirect band gap of 0.47 eV, $MoP_4$ is a topological Dirac semimetal with isolated band crossing at the $\tilde{\Gamma}$ point, and $WP_4$ is a topological nodal line semimetal with a closed nodal ring inside the first BZ. We also make a comparison of the phosphides with group VB and VIIB transition metals and a trend of change from metallic to semiconducting is observed from VB-$MP_4$ to VIIB-$MP_4$ compounds.

### Results and discussion

We first present the structural characterization. Figure 1a shows the structure of monoclinic compounds of $MP_4$ ($M = Cr, Mo, W$) in $C2/c$ ($C_{6h}^2$) symmetry. The $M$ atoms are depicted in black occupying the $4e$ Wyckoff positions, while there are two kinds of $P$ atoms ($P_1$ and $P_2$) depicted in orange occupying two distinct $8f$ Wyckoff positions, respectively, as listed in Table 1. The metals environments in $MP_4$ compounds can be described as the octahedral coordination environment, in which metal atoms are always octahedrally surrounded by $P$ atoms, while $P$ atoms have tetrahedrally coordinated environment. Basically, the crystalline structure of monoclinic $MP_4$ compounds can be seen as a layered structure of black phosphorus in which metal atoms are inserted between two buckled phosphorus layers (Fig. 1b). Metal atoms intercalate and reorder the atomic stacks similar to Na atom insertion in black phosphorus\(^5\). A sandwiched structure is formed where wave like metal atom layers are in between the two buckled phosphorus layers.

There are three unique types of bonds in monoclinic compounds of $MP_4$, namely $M$-$P_1$, $M$-$P_2$, and $P_1$-$P_2$ chemical bonds. In $CrP_4$, the bond lengths are 2.277–2.373 Å for $Cr$-$P_1$, 2.316 Å for $Cr$-$P_2$, and 2.215–2.240 Å for $P_1$-$P_2$; in $MoP_4$, the bond lengths are 2.396–2.456 Å for $Mo$-$P_1$, 2.456 Å for $Mo$-$P_2$, and 2.208–2.243 Å for $P_1$-$P_2$; while in $WP_4$, the bond lengths are 2.398–2.477 Å for $W$-$P_1$, 2.453 Å for $W$-$P_2$, and 2.215–2.245 Å for $P_1$-$P_2$.
there are three distinct types of bond angles depicted as $\angle P_1-M-P_1$, $\angle P_2-M-P_2$ and $\angle P_3-M-P_3$. For CrP$_4$, the bond angles are 90.03° for $\angle P_1-Cr-P_1$, 85.30° for $\angle P_2-Cr-P_2$, and 92.37° for $\angle P_3-Cr-P_3$; for MoP$_4$, the bond angles are 88.19° for $\angle P_1-Mo-P_1$, 83.80° for $\angle P_2-Mo-P_2$, and 94.00° for $\angle P_3-Mo-P_3$; while for WP$_4$, the bond angles are 88.19° for $\angle P_1-W-P_1$, 84.16° for $\angle P_2-W-P_2$, and 93.83° for $\angle P_3-W-P_3$. It can be seen that the bond lengths between P-P atoms are almost same in the three MP$_4$ compounds, while the bond lengths between Mo-P and W-P atoms are clearly larger than that between Cr-P atoms. Meanwhile, $\angle P_1-M-P_2$ are found larger than the other angles in all MP$_4$ compounds. The calculated equilibrium lattice parameters, bond lengths, and bond angles for MP$_4$ compounds are listed in Table 2. It is seen that our calculated structural parameters matches well with the reported experimental and calculated data.

Table 2. Calculated equilibrium lattice parameters ($a$, $b$, $c$ and $\beta$), bond lengths ($d_{M-P_1}$, $d_{M-P_2}$, and $d_{P-P}$), and electronic band gap $E_g$ for MP$_4$ (M = Cr, Mo, W) compounds, comparing with experimental and previously calculated data.

| Compound | Method | $a$(Å) | $b$(Å) | $c$(Å) | $\beta$(°) | $d_{M-P_1}$(Å) | $d_{M-P_2}$(Å) | $d_{P-P}$(Å) | $\angle P-M-P$(°) | $E_g$(eV) |
|----------|--------|--------|--------|--------|-----------|----------------|----------------|----------------|----------------|-----------|
| CrP$_4$  | PBE    | 5.196  | 10.754 | 5.717  | 110.42    | 2.272 - 2.373 | 2.316           | 2.215 - 2.240  | 85.30 - 92.37  | 0.47      |
|          | Exp$^{36}$ | 5.191  | 10.760 | 5.771  | 110.65    |                |                |                |                |           |
|          | PBE$^{38}$ | 5.170  | 10.684 | 5.692  | 110.03    |                |                |                |                | 0.63      |
| MoP$_4$  | PBE    | 5.337  | 11.207 | 5.885  | 110.72    | 2.396 - 2.456  | 2.456           | 2.208 - 2.243  | 83.80 - 94.0   | 0.47      |
|          | Exp$^{36}$ | 5.313  | 11.139 | 5.820  | 110.64    |                |                |                |                |           |
|          | PBE$^{38}$ | 5.268  | 11.090 | 5.798  | 110.80    |                |                |                |                | 0.47      |
| WP$_4$   | PBE    | 5.344  | 11.195 | 5.876  | 110.95    | 2.398 - 2.475  | 2.453           | 2.215 - 2.245  | 84.16 - 93.83  | 0.47      |

Next we discuss the electronic properties of MP$_4$ (M = Cr, Mo, W) compounds. Figure 3 represents the calculated electronic band structures along the high symmetry directions of the BZ using HSE06 functional and the fermi energy ($E_F$) is set to zero. For CrP$_4$ as shown in Fig. 3a, the conduction band minimum (CBM) is located along H-Z direction and valence band maximum (VBM) is located along F-H direction, showing a semiconducting behavior with an indirect band gap of 0.47 eV, which is smaller than the reported direct band gap of 0.63 eV$^{35}$. For MoP$_4$ as shown in Fig. 3b, the lowest conduction band and highest valence band are degenerate at $\Gamma$ point near the $E_F$, indicating that MoP$_4$ is a Dirac semimetal with a four-fold degenerate Dirac point at the $\Gamma$ point$^{41}$. Moreover, our calculations show that the valence and conduction bands of WP$_4$ exhibit linear dispersion near the $E_F$ and cross along the $\Gamma-X$ high symmetry direction (Fig. 3c) due to the band inversion mechanism$^{40}$. To further explore the topological electronic properties, we establish a tight binding (TB) model using the maximally localized Wannier functions (MLWFs)$^{52,53}$ to search the nodal points in the 3D BZ. We find that the nodal points (or band crossing points) of valence and conduction bands in WP$_4$ form a continuous nodal ring in the full BZ (see Fig. 3d), thus, WP$_4$ can be termed as a topological nodal line semimetal with a closed nodal ring protected by $PT$ symmetry$^{34,35,41}$.

It is interesting to notice that although Cr, Mo and W are all in the VIB group of the Periodic Table of Elements, CrP$_4$ is an indirect band gap semiconductor, MoP$_4$ is a Dirac semimetal with a single nodal point, and WP$_4$ is a nodal line semimetal with a closed nodal ring. The metallicity of CrP$_4$, MoP$_4$, and WP$_4$ grows with the increase of the elementary ordinal from 3d to 5d transition metals. To further understand the electronic properties, we have plotted the total and partial density of states (DOS) of MP$_4$ compounds as shown in Fig. 4. For CrP$_4$ (Fig. 4a), there is a band gap of 0.47 eV as depicted in Fig. 3a. The states around the Fermi level are mainly contributed by the p states of P atoms (Fig. 4b), relative to the covalent bonds between P-P atoms. For MoP$_4$ (Fig. 4c), there is a little peak on the Fermi level, the states at the Fermi level are mainly composed of d orbital of Mo atoms (see Fig. 4d). Moreover, for WP$_4$ (Fig. 4e), there is a little peak on the Fermi level, but larger than that in MoP$_4$, the states at the Fermi level are predominantly composed of P-p orbital and W-d orbital (Fig. 4f). It can be inferred that the electronic behaviors in CrP$_4$ are mainly dominated by the P-P covalent bonds in CrP$_4$, so that CrP$_4$ tend to be a semiconductor due to covalent bonding properties between P-P atoms. While in MoP$_4$ and WP$_4$, the electronic properties are largely determined by the metal atoms which have metallic bonds with P atoms, so that they show semimetallic properties. The small peaks on the Fermi level in MoP$_4$ and WP$_4$ semimetals are related to the band touching point between the top of valence and the bottom of conduction bands. Similar DOSs around the Fermi level are also found in CaP$_3$ family of nodal line semimetals$^{41}$.

We have further examined the band structures of MoP$_4$ and WP$_4$ with spin-orbital coupling (SOC) as shown in Fig. S1 in Supplementary Information. For MoP$_4$, the SOC induced band gap is about 0.1 meV at the $\Gamma$ point, while for WP$_4$, the SOC induced band gap is about 29 meV along the high-symmetric X-$\Gamma$ direction. We can
see that when SOC is included, MoP₄ and WP₄ become strong topological insulators with the symmetry-based indicators \((z_2, z_2, z_2, z_4)\) as \((0,0,0,1)\), like as the finding in CaP₃ family of materials\(^4\).

In order to better understand the electronic properties of VIB-MP₄ (\(M = \text{Cr, Mo, W}\)) compounds, we have also examined the electronic properties of the VP₄, NbP₄, TaP₄, MnP₄, TcP₄ and ReP₄, while V, Nb and Ta are in the VB group, and Mn, Tc and Re are in the VIIIB group, which are all next to Cr, Mo and W in the Periodic Table of Elements. The TcP₄ and ReP₄ are experimentally synthesized by the reaction of their constituent elements\(^6\).

The calculated equilibrium lattice parameters and electronic band structures are given in Table S1 and Fig. S2 in Supplementary Information, respectively. The structural parameters and electronic behavior that is, VP₄ is metallic and MnP₄ is a semiconductor reported by Gong et al.\(^5\). We find that VB-MP₄ (\(M = \text{V, Nb, Ta}\)) have metallic behavior, while VIIIB-MP₄ (\(M = \text{Mn, Tc, Re}\)) are semiconductors. It is clearly seen that from VB-MP₄ to VIIIB-MP₄, the metallicity of these phosphides grow weaker with a change from metallic to semiconducting, while from top (3d) to bottom (5d) in each group, the metallicity of these phosphides grow stronger. So it is reasonable that CrP₄ should be a semiconductor, MoP₄ is a semimetal with isolated nodal points and WP₄ is a topological nodal line semimetal with a line of nodes.

**Figure 2.** Phonon band structures and density of states (PDOS) for MP₄ (\(M = \text{Cr, Mo, W}\)) compounds at equilibrium lattice parameters. The lower frequency modes are mainly contributed by the metal atoms because of their heavier masses while the higher frequency modes are mainly contributed by the P atoms with lighter masses.
In conclusion, we have performed a systematic ab initio study on MP$_4$ (M = Cr, Mo, W) monoclinic compounds. Their dynamical stabilities have been confirmed by phonon modes calculations. Electron band structures calculations show that CrP$_4$ is an indirect band gap semiconductor with a narrow band gap of 0.47 eV, MoP$_4$ is Dirac semimetal and WP$_4$ is considered as a new candidate for topological nodal line semimetal with a closed nodal ring in the first BZ protected by the PT symmetry. The electronic density of states calculations indicate that in CrP$_4$, the valence and conduction bands near the Fermi level are mainly contributed by the p orbitals of P atoms, while in MoP$_4$ and WP$_4$, there is little peak on the Fermi level and the energy bands are mainly composed of d orbitals of Mo and W atoms, respectively. We also make a comparison of the phosphides with group VB and VIIB transition metals and a trend of change from metallic to semiconducting is observed from VB-MP$_4$ to VIIB-MP$_4$ compounds. These results provide a systematic understanding and pave the way for further experimental explorations on the transition metal phosphides.

**Methods**

Our calculations were carried out using the density functional theory as implemented in the Vienna ab initio simulation package (VASP)$^{70}$. The projector augmented wave (PAW)$^{71}$ method was adopted with valence electrons of 3s$^2$3p$^4$ for P, 3p$^6$3d$^3$4s$^3$ for Cr, 4p$^6$4d$^5$5s$^5$ for Mo, and 5p$^6$5d$^5$6s$^1$ for W. Generalized gradient approximation (GGA) developed by Perdew, Burke and Ernzerhof (PBE)$^{72}$ is used as the exchange-correlation potential. A 5 × 8 × 6 Monkhorst-Pack grid of BZ sampling is used and an energy cutoff of 500 eV is set for the plane-wave basis. The structures are fully optimized until the total energy difference is less than 10$^{-6}$ eV and convergence criteria for atomic forces is set to be 10$^{-3}$ eV/Å. The electronic properties are calculated with the Heyd–Scuseria–Ernzerhof hybrid functional (HSE06)$^{60}$ and the phonon properties are calculated with phonopy package$^{73}$. To further explore the topological electronic properties, we establish a tight binding (TB) model using the maximally localized Wannier functions (MLWFs)$^{62,63}$ implemented in Wannier90 package$^{74}$ and searched the bandcrossing points in the entire BZ with WannierTools package$^{75}$. 

![Figure 3. Electronic band structures for (a) CrP$_4$, (b) MoP$_4$ and (c) WP$_4$ at equilibrium lattice parameters using HSE06 functional (without spin-orbital coupling). (d) The BZ with several high-symmetry points indicated at Γ(0.00, 0.00, 0.00), Y (0.3067, 0.3067, 0.0440), F (0.3631, 0.3631, 0.3937), H (0.2503, 0.2503, 0.6943), Z (0.00, 0.00, 0.50), I (0.50, −0.50, 0.50), and X (0.50, −0.50, 0.00). The nodal ring (green circle) in (d) is formed by band crossing points for WP$_4$ compound were plotted using MATLAB software.](image-url)
Figure 4. Total and partial density of states (DOS) for MP₄ (M = Cr, Mo, W) compounds at equilibrium lattice parameters using HSE06 functional (without spin-orbital coupling). (a, b) Total and partial DOSs for CrP₄; (c, d) Total and partial DOSs for MoP₄, and (e, f) Total and partial DOSs for WP₄.

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Author contributions
M.R.K. and J.T.W. designed the study and wrote the paper; M.R.K and J.S.C. drawn Fig. 1, M.R.K. calculated the phonon band structures and plot Fig. 2, M.R.K. and K.B. calculated the electronic band structures and plot the Fig. 3, M.R.K. and J.S.C. plot the Fig. 4; all authors discussed the results and contributed to the manuscript.

Competing interests
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