CHIN. PHYS. LETT. Vol. 34, No. 12 (2017) 127101

# Electronic Properties of Defects Induced by H Irradiation in Tantalum Phosphide *

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(Received 9 August 2017)

*Tantalum phosphide (TaP) is predicted to be a kind of topological semimetal. Several defects of TaP induced by H irradiation are studied by the density functional theory. Electronic dispersion curves and density of states of these defects are reported. Various defects have different impacts on the topological properties. Weyl point positions are not affected by most defects. The H atom can tune the Fermi level as an interstitial. The defect of substitutional H on P site does not affect the topological properties. P and Ta vacancies of concentration 1/64 as well as the defect of substitutional H on Ta site destruct part of the Weyl points.*

*PACS: 71.15.Mb, 71.55.Ak, 71.20.Gj* DOI: 10.1088/0256-307X/34/12/127101

Research of topological insulators as well as topological semimetals is very important in low-energy condensed matter physics recently.[1–5] Angle-resolved photon-emission spectroscopy (ARPES) can detect the linear dispersion of surface states in these materials. New technologies and devices can be developed based on these topological materials. Ion beam implantation is a powerful technique to modify properties of materials.[6,7] The modified properties are from defects generated. Defect properties are complicated in regular semiconductors. The modifications are significant for some defects. For example, doping 0.01% atomic percent (low concentration) of boron or phosphorus atoms in silicon can create p-type or n-type silicon. The modifications can be ignored for other defects. For example, co-doping of equal percent of boron and phosphorous atoms in silicon can create intrinsic-like silicon. We call these defects the 'inert' defects. Defects of low concentration are mostly isolated from each other. Defect–defect interactions are small in these cases. Defect–defect interactions are strong at high concentration. Properties of the semiconductor are changed significantly. From the present semiconductor theory, we can predict that properties of defects are also complicated in topological materials. It is interesting to know the defect properties in these topological materials. In comparison of defect properties of semiconductors with topological materials, we can understand more about the band theory of solids. In addition, it is very useful to explore radiation resistant materials. It is interesting to study 'inert' type of defects. Tantalum phosphide (TaP) is predicted to be a kind of topological semimetal.[1,2] Defects are generated by H irradiation in this study. There are 12 pairs of band-crossing points (Weyl points) at the surface of the first Brillouin zone for the perfect TaP. After TaP is exposed to H irradiation, point defects appear. The Weyl points will be affected by the defects. Several kinds of possible point defects include: interstitials ($I_H$), vacancies ($V_P$ and $V_{Ta}$), substitutional H on Ta site ($H_{Ta}$) and substitutional H on P site ($H_P$). The atomic concentrations of defects are all 1/64 in this study. The electronic dispersion curves as well as density of states are calculated by density functional theory.[8–10] The electronic structure differences between defect structures and perfect structure are compared in detail. The defect impacts on topological properties are discussed.

First principle calculations are widely used in condensed matter research.[11] In this work, the first principle calculations are performed using the CASTEP code.[12] Pseudopotentials of GGA (PBE)[13] are employed. Spin–orbit coupling is not considered in the calculation. As shown in Fig. 1 of Ref. [3] Weyl point locations are not affected by spin–orbit coupling interactions. It is easy to determine the corresponding Weyl points in band structures of defects. Cutoff energies are chosen to be 720 eV. The $K$-space meshes in each direction are chosen to be less than 0.02/nm. The energy convergence is set to be less than $0.5\times10^{-5}$ eV.

*Supported by the National Natural Science Foundation of China under Grant Nos 11635003, 11025524, 11675280 and 11161130520, the Fundamental Research Funds for the Central Universities, the National Basic Research Program of China under Grant No 2010CB832903, and the European Commissions 7th Framework Programme (FP7-PEOPLE-2010-IRSES) under Grant No 269131.

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Convergence tests are performed for the above parameters.

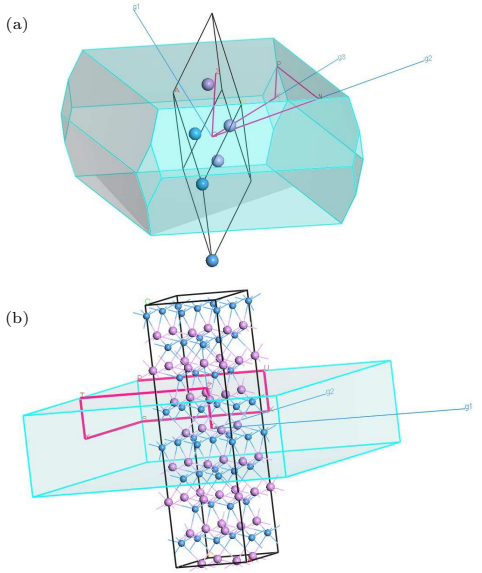


**Fig. 1.** Primitive cell of TaP with symmetry $I4_1md$ (a), supercell of $Ta_{32}P_{32}$ with $Pmm2$ symmetry (b). Ta and P are shown in blue and pink, respectively. The reciprocal lattices are also shown.

Primitive cell of TaP is shown in Fig. 1(a). As shown in Fig. 1(a), the symmetry is $I4_1md$. The optimized lattice parameters are $a = b = c = 0.607$ nm, $\alpha = \beta = 148.5°$, and $\gamma = 45.1°$. To study defects, the cell containing 32 Ta and 32 P atoms are constructed as shown in Fig. 1(b). The optimized unit cell parameters are $a = b = 0.658$ nm, $c = 2.241$ nm, $\alpha = \beta = \gamma = 90.0°$. The corresponding lattice parameters $a = b = 0.664$ nm, $c = 2.268$ nm, $\alpha = \beta = \gamma = 90.0°$ are measured in the experiment.[2] Five typical defects are generated based on the cell shown in Fig. 1(b). We can insert one H atom to the cell center to obtain defect structure $I_H$. We can remove one of the Ta and P atoms in near center of the cell to obtain the two defect structures $V_{Ta}$ and $V_P$. We can substitute one of the Ta and P atoms in near center of the cell by the H atom to obtain the two defect structures $H_{Ta}$ and $H_P$. All the atoms and the cell parameters are relaxed. The lattice parameters are almost the same in all the defect structures. The symmetries are determined by CASTEP to be $Pmm2$ in all the defect structures.

**Table 1.** Defect formation energy of various defects.

| Defect | Formation energy (eV) |
|---|---|
| $I_H$ | −3.13 |
| $V_{Ta}$ | 6.07 |
| $V_P$ | 5.99 |
| $H_{Ta}$ | 0.35 |
| $H_P$ | 0.50 |

As H ions are injected into the TaP sample, various complex defects are formed. Most common defects are vacancies. After the speed of H ions reduced, they can stay in cages or stay in vacancy centers to annihilate the vacancies. The defect formation energies of five typical defects are calculated similar to Ref. [1] and listed in Table 1. The most stable defect is $I_H$. The negative formation energy suggests H atoms are likely to be retained in one of the cages. Vacancies are relatively difficult to form. Substitutional H atoms on P or Ta sites are energetically favorable. H atoms tend to annihilate any vacancies produced.

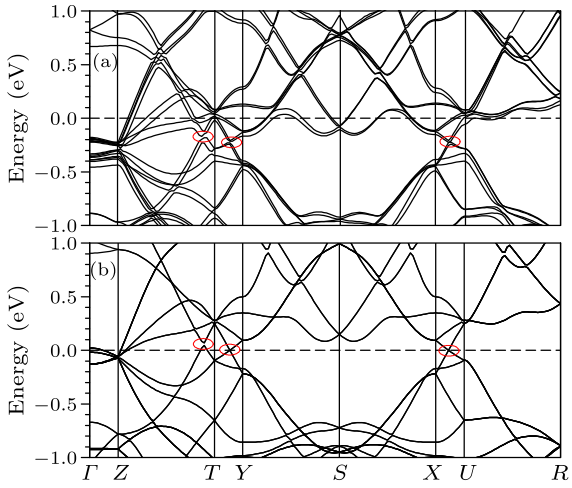


**Fig. 2.** Dispersion curves of $HTa_{32}P_{32}$ (a) and $Ta_{32}P_{32}$ (b). The Fermi level in (a) is almost 0.2 eV above that in (b). The circles indicate the Weyl points.

The five typical kinds of defects are discussed as follows: (1) $I_H$ where H atom is an interstitial atom. Unit cell of this defect structure consists of $HTa_{32}P_{32}$ in this case. The symmetry is $Pmm2$. The H atom is in the center cage of TaP. The dispersion curve is shown in Fig. 2(a). For comparison, the dispersion curve without defects are shown in Fig. 2(b). As shown in Figs. 2(a) and 2(b), the H atom breaks the symmetry of the TaP. The degenerate dispersion curves are separated. As shown in Fig. 2(b), the calculated Weyl point is about 0.58/c at line $T$–$Y$ and is consistent with the experimental measurement.[2] The Weyl points lie on the Fermi level for the perfect TaP. It is found that the positions of the Weyl points are located at their initial places in the Brillouin zone for $I_H$. They are not affected by $I_H$. Fermi level of the $I_H$ defect is raised about 0.2 eV compared with pure TaP. The atomic concentration of H atoms is about 1/65 in this case. The H atom provides an extra electron to the previous TaP bulk system, and the extra electron fills the TaP bulk bands. The bonding network of bulk TaP is stable. The electronic interactions between H and surrounding host atoms are weak. The degenerate bands become nondegenerate as a result of symmetry breaking by the H atom. For all defect structures, the circled points are not exact 'Weyl points'. The degeneracy of the Weyl points is broken by defects. It is reasonable to assume that as the concentration of H

atom reduces, the Fermi energy level raises less. Weyl points are not affected by the low concentration of $I_H$ defect.

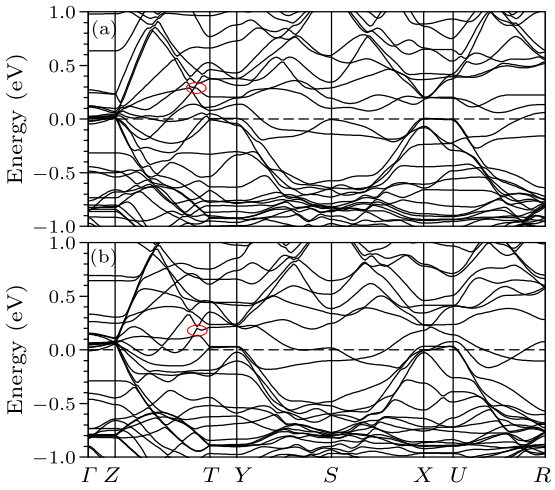


**Fig. 3.** Dispersion curves of $Ta_{31}P_{32}$ (a) and $Ta_{32}P_{31}$ (b). The circles indicate the Weyl points.

(2) $V_{Ta}$ where a Ta atom is removed in the near center of the cell. The dispersion curve of $Ta_{31}P_{32}$ is calculated, as shown in Fig. 3(a). It is shown that the Weyl points within lines $T$–$Y$ and $X$–$U$ disappear. The concentration of Ta vacancy (1/64) is rather high. It is enough to destruct part of the topological properties. The energies at $\Gamma$ point extend to about 0.3 eV near Fermi level. This is different from 0.2 eV for the perfect TaP in Fig. 2(b). This suggests that the symmetry breaking interaction strength of the vacancy is about 0.05 eV. Because of the missing Ta valence electrons, the Fermi level drops. The shift of Fermi level for vacancy and interstitial H are in opposite directions. Weyl points are located at about 0.2 eV above the Fermi level for $V_{Ta}$. The dispersion change is rather large.

(3) $V_P$ where a P atom is removed in the near center of the cell. The dispersion curve of $Ta_{32}P_{31}$ is calculated, as shown in Fig. 3(b). The Fermi level drops in this case. The asymmetry is significant. The band crossings within line $Z$–$T$ exist. The band crossings within lines $T$–$Y$ and $X$–$U$ disappear. Compared with Ta vacancy of the same concentration, the P vacancy affects the topological properties less. The ground state electronic configurations of Ta and P are $[Xe]4f^{14}5d^36s^2$ and $[Ne]3s^23p^3$, respectively. Most known topological insulators and topological semimetals contain at least one heavy element. It is very likely to conclude that the $d$ electrons of Ta are the key for topological properties of TaP. The energies at $\Gamma$ point extend to about 0.3 eV near the Fermi level. This suggests that the symmetry breaking interaction strengths of both vacancies are universal in this material. Because of the missing P valence electrons, the Fermi level drops. Weyl points are located at about 0.2 eV above the Fermi level for $V_{Ta}$. The dispersion change is rather large.

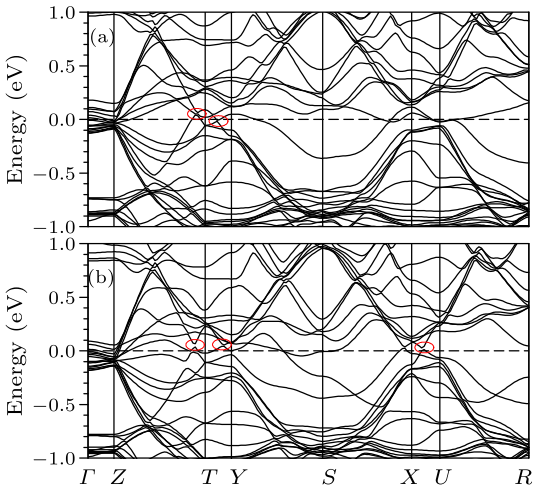


**Fig. 4.** Dispersion curves of $HTa_{31}P_{32}$ (a) and $HTa_{32}P_{31}$ (b). The circles indicate the Weyl points.

(4) $H_{Ta}$ where a Ta atom is substituted by an H atom. The dispersion curve of $HTa_{31}P_{32}$ is calculated, as shown in Fig. 4(a). Compared with Fig. 3(a), the dispersion curves are different. The H atom and vacancy together cannot tune the Fermi level. If the concentration of vacancies and interstitials are close, there is no Fermi level shift effect. The bonding networks of $HTa_{31}P_{32}$ and $Ta_{32}P_{32}$ are the same, while the band crossings within line $X$–$U$ disappear. The vacancy of Ta provides dangling bonds, and the bonds can be healed by the H atom. The topological electronic properties cannot be healed by the H atom in this case. H contains only $s$ electrons. To take out $d$ electrons from one Ta atom in perfect TaP is electronic similar to the defect $H_{Ta}$. The importance of $d$ electrons to topological properties is shown.

(5) $H_P$ where a P atom is substituted by an H atom. The dispersion curve of $HTa_{32}P_{31}$ is calculated as shown in Fig. 4(b). Compared with Fig. 3(b), the band crossings at $Z$–$T$, $T$–$Y$ and $X$–$U$ appear. $H_P$ is one type of the 'inert' defects. The bonding networks of $HTa_{32}P_{31}$ and $Ta_{32}P_{32}$ are the same, and the band crossings properties are almost the same. The vacancy of P provides dangling bonds, the H atom can heal the dangling bonds. The topological electronic properties can also be healed by H atoms in this case. This is recovery of topological properties.[6] The recovery effect is important for the research on radiation resistant materials. To take out $s$ and $p$ electrons from one P atom in perfect TaP is electronic similar to the defect $H_P$. The less importance of $s$ and $p$ electrons to topological properties is shown.

Density of states of various defects are plotted in Fig. 5. The curve of $I_H$ defect is just a horizontal shift from that of TaP. $I_H$ defect does not affect the bulk

band structure too much. The conclusion is consistent with dispersion in Figs. 2(a) and 2(b). As shown in Fig. 5, compared with $V_{Ta}$, density of states for $V_P$ is close to TaP. This suggests that the Ta atom is most important to keep topological properties. $H_{Ta}$ is close to $V_{Ta}$, $H_P$ is close to $V_P$, and the differences of density of states near the Fermi level are small with and without the H atom. It seems that the interstitial H atom raises the Fermi level of bulk TaP. The H atom can fine tune the Fermi level with proper concentrations.

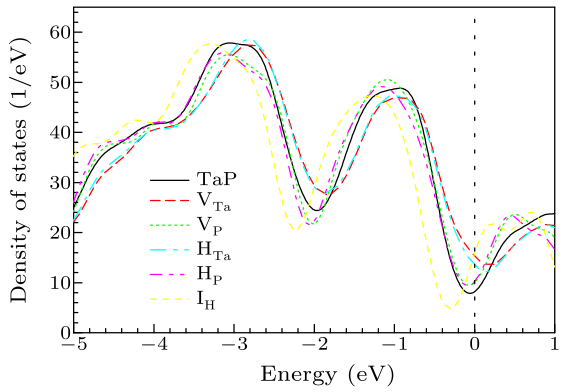


**Fig. 5.** Density of states of various defects.

In summary, various H-induced defects of TaP have been explored theoretically. Various defects have different impacts on the topological properties. Weyl point positions are not affected by defects. Both the vacancies and interstitials can tune the Fermi level. Vacancy tends to disrupt the bulk bands. Substitutional H to vacancy tends to recover the bulk bands. The defect of substitutional H on P site does not affect the topological properties. P and Ta vacancies of concentration 1/64 as well as the defect of substitutional H on Ta site destruct part of the Weyl points.

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