Electronic Structure of Novel Superconductor doped-ZrPSe

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Abstract. In this paper we report the results of the first-principles calculations for cation and anion co-doped system \((Zr_{1-y}Y_y)P(As_{0.25}Se_{0.75})\) using virtual crystal approximation. The density of states at the Fermi level \((=D(E_F))\) shows a dome-shape with respect to the doping concentration \(y\). This result qualitatively explains the observed \(y\) dependence of \(T_c\), especially for \((Zr_{1-y}Y_y)_{1.25}Se_{0.75}\). We also found the similarity of the band structure between ZrSiS and doped-ZrPSe. Characteristic band crossing near \(E_F\), which is found to be the Dirac line node in ZrSiS, is also found in doped-ZrPSe. This result strongly suggests that the superconductivity and the Dirac line node are co-existed in doped-ZrPSe.

1. Introduction

Inspired by the great success of discovering cuprate high-\(T_c\) superconductors, layered structure compounds are energetically developed and investigated. As a result, many high-\(T_c\) superconductors having layered structure are found including MgB₂, hafnium nitrides and iron pnictides/chalcogenides. Recently found superconductor ZrP₂-\(x\)Se\(_x\) [1] has also a layered structure as shown in Fig.1. This crustal structure is called PbFCl-type, and LiFeAs, a kind of iron-based superconductor, has the same crystal structure. The optimum \(T_c\) is about 6.3K, and it becomes even higher when Zr is partially substituted by non-magnetic rare-earth element such as Sc, Y, La and Lu [2]. However, the origin of increasing \(T_c\) was not clear at that time.

Figure 1. Crystal Structure of PbFCl-type ZrP₂Se\(_x\). Blue balls denote Zr atoms, and yellow balls denote the mixture of P and Se atoms. Pink balls denote P atoms forming a square lattice.
We should also note that this structure is retained in a rich variety of compounds ABX (A=Zr, Hf, rare-earth; B=Si, P; X= S, Se). Among them, ZrSiS has a prominent electronic structure which is called Dirac semi-metal (DSM). A first-principles calculation reveals that the Dirac points form a line in three-dimensional momentum space in ZrSiS [3-5]. This Dirac line node has been observed by angle-resolved photoemission spectroscopy [3,4].

This fact immediately reminds us that MgB$_2$ and AlB$_2$ are isostructural, and AlB$_2$ has a Dirac line node [6]. In mixed compound (Mg,Al)B$_2$ we can expect an interplay between superconductivity in MgB$_2$ and topologically non-trivial state in AlB$_2$. From this point of view, investigating the electronic structure of ABX compounds is not only of scientific interests, but may also be important for applications such as quantum computation using non-trivial topological states.

Motivated by the above results, we have performed a systematic *ab-initio* band structure calculation of (Zr$_{1-y}$Y$_y$)P(As$_{0.25}$Se$_{0.75}$) using virtual crystal approximation. We found that the density of states at the Fermi level ($=\Delta(E_F)$) shows a dome-shape with respect to the doping concentration $y$. This result qualitatively explains the observed $y$ dependence of $T_c$, especially for (Zr$_{1-y}$Y$_y$)P(As$_{0.25}$Se$_{0.75}$). We also found the similarity of the band structure between ZrSiS and doped-ZrPSe. Characteristic band crossing near $E_F$ along M-Γ axis, which is found to be the Dirac line node in ZrSiS, is also found in doped-ZrPSe. This result strongly suggests that the superconductivity and the Dirac line node are co-existed in doped-ZrPSe.

This paper is organized as follows: The details of calculations are described in Section 2. The calculated results and the discussions are shown in Section 3. Finally we give some conclusions in Section 4.

2. Methods

One of the simplest theories for handling the mixed crystal is the virtual crystal approximation. We have performed a systematic *ab-initio* band structure calculation of (Zr$_{1-y}$Y$_y$)P(As$_{0.25}$Se$_{0.75}$) using this virtual crystal approximation. Two kinds of virtual atoms are assumed: (i) atom ‘Zy’ (located between $^{40}$Zr and $^{33}$Y) with the electronic charge $Z(y) = 40(1-y) + 39y$, and (ii) atom ‘Ae’ (located between $^{33}$As and $^{34}$Se) with $Z = 33*0.25 + 34*0.75$. This approximation will be justified for dealing with the real compound (Zr$_{1-y}$Y$_y$)P(As$_{0.25}$Se$_{0.75}$) [2] since we checked that the band structure of ZrPSe and ZrAsSe are similar [7]. Once we accept this assumption, we can perform first-principles calculations of this system in a usual way. This calculation is based on the density functional theory (DFT) and the full-potential linearized augmented plane wave method (FLAPW), and the exchange-correlation potential is approximated by general gradient approximation (GGA) [8]. The whole calculation is implemented by the computer code WIEN2k [9]. The space group of this system is P4/mmm (#129), and the unit cell includes two formula units. We used the parameter $RK_{\max}=7.0$, and the muffin-tin radii are set as $r(Zy) = 2.5$, $r(P) = 2.24$ and $r(Ae) = 2.5$ a.u. As for the lattice parameters $a$ and $c$ for each $y$’s, we linearly interpolated the experimental data (assuming Begard’s law) so as to minimize the fluctuation of the observed data. We have also optimized the internal parameter $z_{Zy}$ and $z_{Ae}$ of Zy(1/4, 1/4, $z_{Zy}$) and Ae(1/4, 1/4, $z_{Ae}$) for each $y$ within the above restrictions.

As for the structure optimization and the self-consistent calculation we used the 1000 $k$-points mesh in the 1$^{\text{st}}$ Brillouin zone. Hereafter we show the results for the optimized structure. After convergence of potential, we performed the DOS calculation using 8000 $k$-points mesh. The whole calculation is scalar-relativistic and spin-orbit interaction (SOI) is not included. However, as for $y = 0.15$, in order to discuss the gap opening at the Dirac points we performed additional calculation including SOI as a second variational procedure. We confirmed that the effect of SOI is sufficiently small except in the vicinity of the Dirac points.
For comparison with \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\) system, we also calculated the band structure of ZrSiS. For the crystal structure, we adopted the value written in ref. 3. The obtained band structure well agrees with the previous results [3-5].

3. Results and Discussions

3.1. Density of States

Figure 2. DOS curves of \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\) with \(y = 0, 0.15, 0.25\) and 0.4. The lower panels are the DOS curve of ZrSiS and the \(y\) dependence of \(D(E_F)\). The units of vertical axis are \(\text{eV}^{-1}\) per unit cell (i.e. 2 formula units). In DOS curves, legend “Zr tot” means the DOS projected onto the muffin-tin sphere of Zr (i.e. “total DOS on Zr muffin-tin sphere”). As for finite \(y\), “Zr” should be read as “\(\text{Zy}\)”. Similarly, “Se” should be read as “\(\text{Ae}\)”. See text.

First we show the DOS curve of \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\) with \(y = 0, 0.15, 0.25\) and 0.4 in Figure 2. As is expected, the whole shape of the DOS curve does not change so much with changing \(y\). However, there are two significant differences are found. First, the energy difference between ‘\(\text{Zy-d}\)’ bands and ‘\(\text{Ae-p}\)’ bands increases as \(y\) increases. This is due to the decrease of the effective charge of ‘\(\text{Zy}\)’ atom. Second, the energy of the whole bands is increasing relative to \(E_F\). This is due to the charge of ‘\(\text{Zy}\)’ atom is increasing. Since the latter effect is more effective in the vicinity of \(E_F\), we can adopt a simple rigid-band approximation with respect to the \(y\) dependence of the band structure. There is a small hump at the Fermi energy \((E_F)\) for \(y = 0.15\). Scanning this \(y\) value, we can see that this hump goes through \(E_F\). Eventually, the DOS at \(E_F\) (=\(D(E_F)\)) shows a ‘dome shape’ with respect to \(y\). Considering that \(T_c\) is a monotonic function of \(D(E_F)\) in the BCS theory, this behavior qualitatively explains the observed \(y\) dependence of \(T_c\) in \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\). However, in other doped system \((\text{Zr}_{1-y}\text{Sc}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\), for example, this agreement is not well [2]. Experimentally, the maximum \(T_c\) is
obtained for $y = 0.25$. This may show the limit of the virtual crystal approximation. Sc-d band is usually much higher in energy than Y-d band, so the state near $E_F$ is considered to be quite different.

Next we compare the DOS curve of $(Zr_{1-y}Y_y)P(As_{0.25}Se_{0.75})$ and ZrSiS. If we set $y = 0$ then the former becomes ZrP(As$_{0.25}$Se$_{0.75}$). We can see that the conduction band is rather similar. As for the valence band, three prominent differences are found. First, the peak of the ‘As’ (=As$_{0.25}$Se$_{0.75}$) p band in ZrP(As$_{0.25}$Se$_{0.75}$) (with energy $\sim -3$ eV) has about 1 eV higher energy than that of S-p band in ZrSiS. This is explained by the deeper orbital energy of S-p than that of Se-p. Mixing As for Se further increases the orbital energy. Anyway, these states have negligible contribution to the states in vicinity of $E_F$. More important difference is that the peak energy of P-p in ZrP(As$_{0.25}$Se$_{0.75}$) (broad peak with energy $\sim -3$ eV) and Si-p in ZrSiS (with energy $\sim -2$ eV). Interestingly, in ZrP(As$_{0.25}$Se$_{0.75}$) these states are well extended in energy, and have considerable contribution at $E_F$. In fact, we can see that ZrP(As$_{0.25}$Se$_{0.75}$) has more bands crossing $E_F$ than ZrSiS, shown in the following subsection. Finally, ZrSiS has a large dip in DOS curve at $E_F$. This makes $D(E_F)$ of ZrSiS very small, and highlights the importance of the Dirac points in ZrSiS.

### 3.2. Energy Band Dispersion and Fermi Surfaces

Next we discuss the energy band dispersion of $(Zr_{1-y}Y_y)P(As_{0.25}Se_{0.75})$ in vicinity of $E_F$. Figure 3 is the result for $y = 0.15$, which experimentally shows the maximum $T_c$, and which shows the maximum $D(E_F)$ in this calculation. For comparison, we also show the band dispersion of ZrSiS. We can clearly see that the band dispersion has many similarities between these two panels. Both compounds have Dirac points along M- $\Gamma$ and A-Z axes, as shown in ovals in Fig.3. There are two kinds of Dirac points. One is on the high symmetry k-point such as X and Z shown in Fig.3 with dashed ovals. On these points, the degeneracy is protected by the non-symmetric glide symmetry and SOI cannot lift this degeneracy. The other is not on these high symmetry point, and this degeneracy is lifted by SOI and a small gap opens. The magnitude of this SOI gap at the Dirac points along M- $\Gamma$ and A-Z axes (shown in solid ovals) is $\sim 20$ meV both for $(Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})$ and ZrSiS.

However, mainly two differences can be seen. First, $(Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})$ has ‘extra bands’ near $E_F$. As shown in the previous subsection, the P-p band in $(Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})$ is quite broader than the Si-p band in ZrSiS. In Fig.3 we show the contribution of P-p or Si-p orbitals by the ‘fatness’ of the band. We can clearly see several ‘fat’ bands in $(Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})$, while in ZrSiS there is no such a band in this energy region. We also note that the other bands are mostly consist of Zr-d orbitals.

![Energy Band Dispersion](image-url)
Figure 3. Energy dispersion curves of \((Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})\) and ZrSiS near \(E_F\). The units of vertical axis are eV. The fatness of the line shows the contribution of P-p or Si-p orbitals. Ovals show a typical Dirac point.

Finally we discuss the Fermi surfaces (FSs) of \((Zr_{1-y}Y_y)P(As_{0.25}Se_{0.75})\). Although the band structure looks complicated, the number of FSs is only two (shown in the lower and upper panels) for every composition \(y\). The most characteristic feature is the two (large and small) diamond-shape FSs shown in the upper panels. These FSs are highly two-dimensional. At \(y = 0\) the outer (larger) FS is centered at M point (the corner of the Brillouin zone), but at \(y = 0.4\), this FS changes its topology and centered at \(\Gamma\) point. Interestingly, a van-Hove singularity (saddle point) is seen in X point. As seen in the band dispersion curve (Fig.3), this outer FS mainly comes from P-p orbitals (‘extra band’), considerably hybridized with Zr-d orbitals. On the other hand, the inner (smaller) FS of the upper panel is related to the Dirac point. In ZrSiS there is no ‘extra band’, so only this inner FS is observed [3,4]. The lower panels are other FSs, mostly hole pocket at X point and three-dimensional small electron pocket at \(\Gamma\) point for small \(y\). We cannot determine which FS is relevant for superconductivity at this moment. However, if the outer FS of the upper panel is relevant, then the characteristic square lattice of the P atom (seen in Fig.1) plays an important role for superconductivity, and is very interesting. Observation of these FSs and further theoretical analysis are the future works.

Figure 4. Top view \(=(k_x,k_y)\) plane of the Fermi surfaces of \((Zr_{0.85}Y_{0.15})P(As_{0.25}Se_{0.75})\). Boldness of the curve represents the band dispersion along \(k_z\)-axis.
4. Conclusion

We have calculated the band structure of novel superconductor \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\) from first-principles using this virtual crystal approximation. Experimentally observed dome-shaped \(y\)-dependence of \(T_c\) is qualitatively explained by the change of DOS at the Fermi energy. The Dirac line nodes found in isostructural compound \(\text{ZrSIS}\) is also found in \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\). In addition to the band forming the Dirac line node, another band crosses the Fermi level in \((\text{Zr}_{1-y}\text{Y}_y)\text{P(As}_{0.25}\text{Se}_{0.75})\). This band structure suggests that superconducting \((\text{Zr}_{1-y}\text{Y}_y)\text{P}_{2-x}\text{Se}_x\) is a promising candidate to have topological state.

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