Electronic Structure of Novel Non-centrosymmetric Superconductor Mg$_2$Rh$_3$P

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Abstract. We calculated the electronic structure of a novel non-centrosymmetric superconductor Mg$_3$Rh$_3$P from first-principles. Stoichiometric Mg$_3$Rh$_3$P shows a pseudogap at the Fermi level. This is consistent with the experimental fact that the stoichiometric sample Mg$_3$Rh$_3$P does not show superconductivity and the Mg-deficient sample Mg$_{1.9}$Rh$_3$P shows superconductivity with $T_c \sim 3.6$ K. The band dispersion of Mg$_3$Rh$_3$P shows a characteristic band splitting due to the anti-symmetric spin-orbit coupling (ASOC). The magnitude of ASOC of Mg$_3$Rh$_3$P is comparable to Li$_2$Pd$_3$B. We also show that its 5d-counterpart Mg$_3$Ir$_3$P may have quite a large ASOC, and is a good candidate of parity-mixed superconductor likewise Li$_2$Pd$_3$B.

1. Introduction

The non-centrosymmetric (i.e. without space inversion symmetry) superconductors have been paid much attention because they can exhibit anomalous parity-mixed superconducting state [1,2]. Among them, Li$_2$M$_1$B (M = Pd, Pt) are one of the most energetically studied compounds [3-12]. NMR experiment shows that the superconducting state of Li$_2$Pt$_3$B includes considerable spin-triplet component [5], while in Li$_2$Pd$_3$B it seems to be spin-singlet. However, for both compounds the symmetry of the order parameter is still controversial. The large upper critical magnetic field ($H_{c2} \sim 4$ T) of Li$_2$Pt$_3$B also indicates that the Cooper pair forms the spin-triplet state [6]. This large $H_{c2}$ is also advantageous for various applications. The difference between Li$_2$Pd$_3$B and Li$_2$Pt$_3$B has been explained as follows: In the non-centrosymmetric crystals, spin-orbit interaction (SOI) has an asymmetric component, and it causes a characteristic parity mixing. Since Pt-5d orbitals has larger SOI than Pd-4d orbitals, Li$_2$Pd$_3$B has a large parity mixing while Li$_2$Pd$_3$B does not have such anomaly.

Recently we have discovered a new ternary superconductor Mg$_{2.8}$Rh$_3$P, which has the non-centrosymmetric crystal structure similar to Li$_2$M$_1$B [13]. The detail of the symmetry of the order parameter has not been clear yet. Interestingly, stoichiometric sample Mg$_3$Rh$_3$P does not show superconductivity above 1.8K, and about 5% deficiency of Mg leads to the superconducting phase with $T_c \sim 3.6$ K. These experimental results immediately invoke us two questions: First, is the parity mixing in Mg$_{2.9}$Rh$_3$P large or not? How about the 5d-counterpart compound, Mg$_3$Ir$_3$P (which is not synthesized yet)? Second, why the stoichiometric sample Mg$_3$Rh$_3$P does not show superconductivity while Mg-deficient sample Mg$_{1.9}$Rh$_3$P show superconductivity?
In order to answer these questions, we have performed an *ab-initio* band structure calculation of Mg$_2$Rh$_3$P and Mg$_2$Ir$_3$P. 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.

We found that Mg$_2$Rh$_3$P has a pseudogap at the Fermi level ($E_F$). About 10% Mg deficiency shifts $E_F$ and increases DOS drastically, which can explain the above-mentioned experimental result. On the other hand, Mg$_2$Ir$_3$P has a large DOS at $E_F$ in the stoichiometric form.

2. Methods

We have calculated the electronic structure of Mg$_2$Rh$_3$P and Mg$_2$Ir$_3$P from first-principles. 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) [14]. The whole calculation is implemented by the computer code WIEN2k [15]. The unit cell includes four formula unit, i.e., $Z = 4$. We used the parameter $RK_{\text{max}} = 7.0$, and the muffin-tin radii are set as $r$(Mg) = 2.37, $r$(Rh/Ir) = 2.36 and $r$(P) = 1.83 a.u. As for Mg$_2$Rh$_3$P, we used the experimentally determined lattice parameter ($a = 7.0905$ Å) and space group (#213, P4$_3$32). This space group is enantiomorphic with the space group of Li$_2$Pt$_3$B, which is denoted as P4$_3$32 (#212). These two space groups are the same except the helicity. We have also optimized the internal parameter $x$ of Mg($x$, $x$, $x$) and $y$ of Rh(1/8, $y$, $y$+1/4) within the above restrictions. We obtained $x = 0.04062$ and $y = 0.17794$, which agrees well with the experimental value ($x_{\text{exp}} = 0.0397$ and $y_{\text{exp}} = 0.1818$). As for Mg$_2$Ir$_3$P, we assumed the same lattice constant and space group as Mg$_2$Rh$_3$P, and performed an optimization of the internal parameter $x$ and $y$. We obtained $x = 0.04009$ and $y = 0.17465$, which are very close to those of Mg$_2$Rh$_3$P. As for the structure optimization and the self-consistent calculation we used the 1000 $k$-points mesh in the 1st 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. Spin-orbit interaction (SOI) has been included by a second-variational approach in this calculation.

3. Results and Discussions

![Figure 1. DOS curves of Mg$_2$Rh$_3$P and Mg$_2$Ir$_3$P. The right panels are blow-ups near $E_F$. The units of vertical axis are eV$^{-1}$ per unit cell (i.e. 4 Mg$_2$Rh$_3$P).](image-url)
First we show the DOS curve of Mg$_2$Rh$_3$P and Mg$_2$Ir$_3$P in figure 1. Since they are isovalent, the shape of DOS curves is very similar. The valence bands mostly consist of Rh/Ir-d orbitals, and P-p orbitals are strongly hybridized with them. The width of the valence band (below $E_F$) is 7.1 eV for Mg$_2$Rh$_3$P and 8.8 eV for Mg$_2$Ir$_3$P. This is mainly because Rh4d orbitals are more localized than Ir5d orbitals. This behavior is also seen in Li$_2$Pd$_3$B and Li$_2$Pt$_3$B. The width of the valence band of Li$_2$Pt$_3$B is about 20% larger than that of Li$_2$Pd$_3$B [4].

The right panels are the blow-up near $E_F$. We can clearly see that Mg$_2$Rh$_3$P has a pseudogap near $E_F$. This extremely small DOS is apparently disadvantageous for superconductivity.

Next we discuss the electronic structure of Mg$_{1.9}$Rh$_3$P. As discussed above, the valence bands mostly consist of Rh-d and P-p orbitals, and Mg-s and Mg-p orbitals have a negligible contribution. Therefore, we can look Mg$_2$Rh$_3$P as a Zintl phase, like [Mg$_{2+}$]$_4$[Rh$_3$P]$_4$. According to this picture, Mg-deficient phase Mg$_{1.9}$Rh$_3$P can be described as [Mg$^{2+}$]$_{1.9}$[Rh$_3$P]$_{3.8}$. That is, Mg deficiency gives a 0.2 e hole doping per formula unit to the valence band. In the rigid-band picture, this effect is described as a shift of $E_F$. The shifted $E_F$ is shown by the dotted vertical line in the upper-right panel. This shift drastically increases DOS as twice or more. This behavior gives a natural explanation of the experimental fact that stoichiometric Mg$_2$Rh$_3$P does not show superconductivity, and Mg-deficient Mg$_{1.9}$Rh$_3$P shows superconductivity.

On the other hand, Mg$_2$Ir$_3$P may have different properties. Similar to Mg$_2$Rh$_3$P, the DOS of Mg$_2$Ir$_3$P has a large dip at $E_F$. However, there is still a large amount of the residual DOS. Therefore, we can expect that Mg$_2$Ir$_3$P will be superconducting in the stoichiometric composition.

![Figure 2. Energy dispersion curves of Mg$_2$Rh$_3$P and Mg$_2$Ir$_3$P near $E_F$. The units of vertical axis are eV. The upper (lower) panels are the calculated results without (with) including SOI. Circles show a typical band splitting due to ASOC.](image-url)
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