Electronic structures and effective models in BaPtSb and BaPtAs with ordered honeycomb structures

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Abstract. We investigate the low-energy electronic properties and construct the effective model Hamiltonians in the normal state for new materials BaPtSb and BaPtAs with ordered honeycomb structures. The preliminary experimental study suggested that the former compound may be a candidate of the time-reversal symmetry breaking superconductors. The low-energy electronic structures obtained from the first principles calculation mainly consist of Pt 5\textit{d} and Sb/As 5\textit{p}/4\textit{p} orbitals, where there exist the strong hybridizations between both orbitals. We show that the main parts in the low-energy region including the Fermi surface are well described using renormalized 3 bands consisting of dominant Pt 2 bands and Sb/As 1 band. Our result provides a starting point for microscopic investigation in the superconducting states for the materials with the hexagonal structure.

1. Introduction
The time-reversal symmetry breaking (TRSB) superconductors have received special interest for their intriguing properties in the fields of the topological condensed matter and the strongly correlated electron systems. It is well known that the hexagonal lattice structure favors the realization of the TRSB superconducting states. The intrinsic spontaneous magnetic fields are observed in the superconducting phase in the typical material SrPtAs in the hexagonal KZnAs-type structure [1, 2]. Recently, new materials BaPtSb and BaPtAs in the SrPtSb-type structure show superconducting states [3, 4], whose lattice structures are similar to that of SrPtAs. In particular, the preliminary experimental study for BaPtSb observed the occurrence of the spontaneous magnetic field in the superconducting phase, which indicated that the superconducting state in BaPtSb may break time reversal symmetry [5].

In the present study, to identify the low-energy electronic properties microscopically, we investigate the electronic states of BaPtSb and BaPtAs in the normal phase and construct the effective model Hamiltonians by means of the first principles method and the tight-binding approach.

2. Electronic structures from first principles calculation
In order to obtain the electronic structures of BaPtSb and BaPtAs, calculations are carried out by using the Quantum Espresso Package [6, 7] based on the plane wave pseudopotential method. We employ 24 × 24 × 12 \textit{k}-point mesh in the Brillouin zone for both materials, and the kinetic energy cutoff for wavefunctions is set to 80 Ryd.
Figure 1. Electronic structures obtained from the first principles method for BaPtSb (left panel) and BaPtAs (right panel). The black (red) lines denote the corresponding bands without (with) the SO interaction.

The lattice structures of BaPtSb and BaPtAs have the SrPtSb-type one with space group $P\bar{6}m2$ (No. 187). The lattice constants obtained experimentally are $a = 4.535\,\text{Å}$, $c = 4.884\,\text{Å}$ for BaPtSb [8], and $a = 4.308\,\text{Å}$, $c = 4.761\,\text{Å}$ for BaPtAs [4], respectively.

We first perform the optimization for all lattice parameters. The obtained lattice constants including effects of the spin-orbit (SO) interaction are $a = 4.605\,\text{Å}$, $c = 4.906\,\text{Å}$ for BaPtSb, and $a = 4.356\,\text{Å}$, $c = 4.800\,\text{Å}$ for BaPtAs as the most stable states. In comparison with the experimental results, the maximum difference of lattice parameters is within 1.6%.

The band structures of BaPtSb and BaPtAs for the most stable lattice parameters are depicted in Fig. 1. Both band structures are almost identical qualitatively in the low energy region except M point. Note that while the energy eigenvalues for BaPtSb around M point touch the Fermi level, those for BaPtAs are slightly below the Fermi level.

In order to clarify the contribution of each orbital in the low-energy region, we show the Density of States (DOS) and the band structure with the projected weights of Pt $5d$ and Sb $5p$ orbitals for BaPtSb without the SO interaction in Fig. 2. The DOS around the Fermi level is mainly derived from Pt $5d$ and Sb $5p$ orbitals, where both contributions are comparable.

Note that the energy eigenvalues are divided into two groups, \{Pt ($d_{x^2-y^2}$, $d_{xy}$), Sb ($p_x$, $p_y$)\} and \{Pt ($d_{yz}$, $d_{zx}$), Sb ($p_z$)\}, shown in Fig. 2 right panel. There exist the strong hybridizations between those orbitals in the same groups. The main part of energy eigenvalues of the Pt $d_{3z^2-r^2}$ orbital is far from the Fermi level. Similar results for BaPtAs are also obtained.

Figure 2. (Left panel) Total and partial DOSs of Pt $5d$ and Sb $5p$ orbitals for BaPtSb. (Right panel) The band structure with projected weights of Pt $5d$ and Sb $5p$ orbitals without the SO interaction.
3. Construction of effective models

In this section, we construct the effective models based on the results from the first principles calculation, which becomes a point of departure to investigate the superconducting state and other physical properties microscopically for both materials.

We focus on the low-energy electronic structure around the Fermi level which affects strongly the physical properties such as superconductivity. In the previous section, we showed the low-energy bands consist of two groups, \{Pt \((d_{x^2-y^2}, d_{xy})\), Sb \((p_x, p_y)\)\} and \{Pt \((d_{yz}, d_{xz})\), Sb/As \(p_z\)\}. Although they have the strongly hybridizations in the same groups, the weights of Pt \(d_{x^2-y^2}\), \(d_{xy}\), and Sb/As \(p_z\) orbitals are comparatively larger than the other orbitals in each group. Thus, we focus on the following three orbitals Pt \(d_{x^2-y^2}\), \(d_{xy}\), and Sb/As \(p_z\), for simplicity. Note that some of Wannier functions obtained from the Wannier90 package \([9]\) spread over the Pt and Sb/As sites widely, which indicates that the electrons hop long distances with those basis.

We here construct the 3 band tight-binding model by means of the Slater-Koster approach \([10]\). The lattice structure is defined by the primitive translation vectors \(a_1 = (a, 0, 0)\), \(a_2 = \left(-\frac{a}{2}, \frac{\sqrt{3}a}{2}, 0\right)\), \(a_3 = (0, 0, c)\) where \(a\) (\(c\)) denotes the lattice constant in the \(a-b\) plane (along the \(c\) axis). Sb/As (Pt) site in the unit cell is specified with \(\tau_{\text{Sb/As}} = (0, 0, 0)\) \((\tau_{\text{Pt}} = \left(\frac{a}{2}, \frac{a}{2\sqrt{3}}, 0\right)\)). The diagonal SO interactions concerning the spin and orbital are added to the model in the \(a-b\) plane, for simplicity.

Then the Hamiltonian is given by

\[
H = \sum_k \sum_{m,m'} \sum_{\sigma,\sigma'} \varepsilon_k^{(m\sigma,m'\sigma')} c_{k,m\sigma}^\dagger c_{k,m'\sigma'},
\]

where \(c_{i,m\sigma}^\dagger\) (\(c_{i,m\sigma}\)) is the creation (annihilation) operator for electrons on the site \(i\), in the orbital \(m\) (Pt \(d_{x^2-y^2}\), \(d_{xy}\), and Sb/As \(p_z\)) with the spin \(\sigma\). \(t_{ij}^{mm'}\) stands for the hopping obtained from the Slater-Koster approach. \(r_i, k, \lambda_m,\) and \(\epsilon_m\) denote the position of the unit cell, the wave vector, the amplitude of the SO interaction, and the on-site potential. \(T_l\) stands for the nearest neighbor vector in the \(a-b\) plane between same atoms with \(T_l = \{a_1, a_2, a_1 + a_2\}\).

Diagonalizing Eqn. (2), we obtain the energy eigenvalues concerning BaPtSb, which is shown in Fig. 3. The on-site potentials are \(-0.80\) (Pt) and \(-0.48\) (Sb), and the amplitudes of the SO interaction are \(\lambda_m = 0.02\) for all orbitals, respectively. The hopping parameters between the nearest neighbor (NN), the next nearest neighbor (NNN), and the 3rd nearest neighbor (3NN) are given in Table 1, where \((\alpha\beta m)\) represents the hopping amplitude depending on the

![Figure 3. Energy eigenvalues for BaPtSb without/with the SO interaction.](image-url)
Pt-Pt

|          | (ddσ) | (ddπ) | (ddδ) | (ddσ) | (ddπ) | (ddδ) | (ddσ) | (ddπ) | (ddδ) |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| a-b plane | NN     | 0.60   | 0.15   | 0.05   | NNN    | −0.1   | 0.05   | 0.02   | 3NN    | 0.15   | 0.03   | 0.02   |
| c axis   | NN     | 0.05   | 0.05   | 0.05   | NNN    | −0.05  | −0.05  | 0.00   | 3NN    | 0.05   | −0.02  | 0.00   |

Sb-Sb

|          | (ppσ) | (ppπ) | (ppσ) | (ppπ) |
|----------|--------|--------|--------|--------|
| a-b plane | NN     | −0.30  | −0.20  | NNN    |
| c axis   | NN     | 0.20   | 0.02   | NNN    |

Pt-Sb

|          | (pdσ) | (pdπ) | (pdσ) | (pdπ) |
|----------|--------|--------|--------|--------|
| a-b plane | NN     | −0.30  | 0.20   | NNN    |
| c axis   | NN     | −0.05  | 0.05   | 3NN    |

Table 1. Hopping parameters in the a-b plane and along the c axis between Pt-Pt, Sb-Sb, and Pt-Sb sites.

distance between the orbitals α and β with the component of angular momentum \( m \) around the quantization axis. The hopping between Pt-Sb sites vanishes in the a-b plane due to the lattice symmetry, and those along the c axis direction remain.

The obtained eigenvalues capture features of the result for BaPtSb from the first principles calculation around the Fermi level qualitatively. For BaPtAs, the similar procedure gives the effective model. This result indicates that the low-energy electronic structure is well described by the 3 band model, and the effect from eliminated orbitals is renormalized partially in the hopping parameters.

4. Summary and discussion

We have investigated the electronic structure of BaPtSb and BaPtAs and constructed the effective models with the first principles method and the tight-binding approach. We show that the low-energy electronic structures are dominated by the Pt 5d and Sb/As 5p/4p orbitals, and the effective model Hamiltonians are well described by Pt \( d_{x^2−y^2}, d_{xy} \), and Sb/Ab \( p_z \) orbitals.

While these materials constitute the ordered honeycomb network in the a-b plane, the lattice parameters \( a \) and \( c \) are comparable. The obtained result shows that the hopping along the c axis as well as those in the a-b plane may affect physical properties. The diagonal SO interactions concerning the spin and orbital in the present study may give rise to the metallic state with the spin-Hall effect though the Pt-Sb hopping along the c axis.

[1] Nishikubo Y, et al. 2011 J. Phys. Soc. Jpn. 80 055002.
[2] Biswas P K, et al. 2013 Phys. Rev. B 87 180503 (R).
[3] Kudo K, et al. 2018 J. Phys. Soc. Jpn. 87 063702.
[4] Kudo K, et al. 2018 J. Phys. Soc. Jpn. 87 073708.
[5] Adachi T, et al. 2018 KEK-MSL REPORT 2017 54.
[6] Giannozzi P, et al. 2009 J. Phys.:Condens. Matter 21 95502.
[7] Giannozzi P, et al. 2017 J. Phys.:Condens. Matter 29 465901.
[8] Wenski G and Mewis A 1986 Z. Anorg. Allg. Chem. 535 110.
[9] Mostofi A A, et al. 2014 Computer Physics Communications 185 2309.
[10] Slater J C and Koster G F 1954 Phys. Rev. 94 1498.