Band structure of superconducting Dirac electron systems

Takahiro Kuraya and Yuki Fuseya
Department of Engineering Science, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
E-mail: kuraya@kookai.pc.uec.ac.jp

Abstract. The band structures of PbTe and SnTe are theoretically investigated. First-principles calculation is carried out on the basis of the density functional theory within the generalized gradient approximations. Then, in order to study the fine band structures in the low energy region, the tight-binding model is introduced based on the most localized Wannier functions derived from the first-principles calculations. It is found that the topology of the equal energy surface is different between PbTe and SnTe due to the spin-orbit interaction. The information of the topologically different Fermi surface will be important to study the superconducting mechanism on doped PbTe and SnTe.

1. Introduction
The narrow gap IV-VI semiconductors, such as PbTe and SnTe, are famous for their highly efficient thermoelectricity [1]. Although they are semiconductors stoichiometrically, they exhibit clear evidence for the existence of Fermi surfaces without any doping [2]. Moreover, PbTe and SnTe become superconductors by doping. The latter exhibits superconductivity by self-doping, As and Sb counter doping [3] and In doping [4]. The former exhibits superconductivity by Tl doping [5], though it has not exhibited superconductivity by self-doping.

The band structures of these compounds have been investigated repeatedly. Some of them are done by first-principles calculations [6, 7, 8] and some of them by linear combination of atomic orbital (LCAO) calculations [9]. Since the energy gap of IV-VI semiconductors are very small ($E_{\text{gap}} = 0.186$ eV for PbTe [10] and $E_{\text{gap}} \approx 0.3$ eV for SnTe [11]), the accuracy of first-principles calculations are not enough and it is hard to obtain information of fine band structure. On the other hand, LCAO calculations can tune the parameters so as to fit with experimental data and can investigate fine band structures, but theoretical grounds for the parameters are not so reliable.

In the present work, we carry out first-principles calculations for PbTe and SnTe, and then lead to the tight-binding model on a basis of the most localized Wannier functions derived from the first-principles calculations. With this scheme, we can investigate the fine band structure with parameters determined ab initio, namely, our scheme has both strong points of first-principles and LCAO calculations.
2. Band structures

We carried out the first-principles calculations based on the density-functional theory within the generalized gradient approximation (GGA) using the OpenMX code [12, 13, 14], where the core Coulomb potential is replaced by norm-conserving pseudopotentials and pseudo-atomic orbitals (PAOs) are used as basis functions to expand one-particle Kohn-Sham wave functions. In the following, the PAO basis functions are chosen as Pb10s1p1d1, Sb9s1p1d1, Te9s1p1d1, where the number implies the cutoff radius of the PAO functions and s1p1d1 means that one primitive orbitals for each $s$, $p$, and $d$-orbitals are used for PAO basis functions. The $k$-point sampling for the fist-principles calculation is $12 \times 12 \times 12$ and that for the tight-binding calculation is $200 \times 200 \times 200=2$ in the first Brillouin zone.

The band structures obtained by the first-principles calculation for PbTe and SnTe are shown as the solid lines in Fig. 1. The results obtained by the tight-binding model on the basis of the most localized Wannier functions derived from the first-principle calculations are also shown as the dotted lines in Fig. 1. The tight-binding results agree quite well with those by the first-principles calculations.

The global features are consistent with previous works [6, 7, 8, 9]. The minimum of the conduction band and the maximum of the valence band locate at the $L$-point. The energy gaps are $\Delta_{\text{Pb}} = 0.115$ eV and $\Delta_{\text{Sn}} = 0.280$ eV, which are close to experimental values. The second maximum of the valence band appear close to the midpoint of the $\Gamma$-$K$ lines. Here we denote the position of the second maximum of the valence band in the $\Gamma$-$K$ line as $\Sigma_0$. Basically, the upper three bands originate from three $p$-orbitals of anion (Te) and the lower three bands originate from three $p$-orbitals of cation (Pb, Sn). However, they are hybridized due to the strong spin-orbit interactions. It should be noted that, for PbTe, the lowest conduction band and the highest valence band are strongly coupled and isolated from the other bands. In such a case, the so-called Wolff Hamiltonian, which is essentially equivalent to the Dirac Hamiltonian but with spatial anisotropy, should be a good effective Hamiltonian [15, 16]. On the other hand, for SnTe, the other two conduction bands are close to the lowest conduction bands. Thus there should be relevant couplings between four bands besides the coupling between the lowest conduction and the highest valence bands. This “tug-of-war” between bands leads to the relatively flat band for the lowest conduction band of SnTe.
In the low energy region, $|E| < 1$ eV, there is an important difference between PbTe and SnTe; the energy difference between the $L$- and $\Sigma_0$-point of the highest valence band. The energy difference for SnTe, $E_L - E_{\Sigma_0} = 201$ meV, is about twice larger than that of PbTe, $E_L - E_{\Sigma_0} = 104$ meV. This is a quantitative difference, but can generate a qualitative difference for the Fermi surface as discussed later.

**Figure 2.** Band structures for PbTe (left) and SnTe (right) obtained by the tight-binding model on the basis of the most localized Wannier functions derived from first-principles calculations.

In Fig. 2, the band structures with (solid lines) and without (dotted lines) the spin-orbit interaction (SOI) are shown. It is clearly seen that the band structure of PbTe is modified a great deal by the SOI, while that of SnTe is not so much. These differences can be easily understood if we consider the atomic SOI of Pb ($\sim 1.35$ eV) and Sn ($\sim 0.45$ eV). It is interesting that the band gap at the $L$-point of PbTe is greatly reduced by the SOI from 0.840 eV to 0.115 eV, while that of SnTe is slightly enhanced from 0.0409 eV to 0.289 eV. According to Ref. [6], the highest valence (lowest conduction) band has $L_6^+$ ($L_6^-$) symmetry both for PbTe and SnTe when the SOI is absent. Basically, the SOI lowers the $L_6^-$ band and lifts up the $L_6^+$ band [17], so that the band gap decreases as is seen in PbTe. In SnTe, however, since the gap without SOI in small, the gap first decreases, and then increases after the band inversion between $L_6^+$ and $L_6^-$. An important difference appears at the $\Sigma_0$ point. The energy at the $\Sigma_0$ of Pb/Te is enhanced from -0.645 eV to -0.179 eV, while that of SnTe is not changed so much.

The difference between PbTe and SnTe can be seen more clearly from the virtual crystal approximation (VCA) for Pb$_{1-x}$Sn$_x$, where the tight-binding parameters are linearly extrapolated between PbTe and SnTe, as is shown in Fig. 3. At the $L$-point, the top of the valence band hardly changes as Sn content ($x$) increases in the case with the SOI (the left panel of Fig. 3). The energy decrease is less than 20 meV. In the case without the SOI, on the other hand, the energy at the $L$-point rapidly increases by $x$ for more than 400 meV. Therefore, the top of the valence band is pinned due to the SOI. In contrast, at the $\Sigma_0$-point, the top of the band rapidly decreases as $x$ decreases in the case with the SOI and it increases without the SOI. The energy decrease is about 114 meV for the case with SOI, and the energy increase is about 207 meV for the case without SOI. Hence, the top of the band at the $\Sigma_0$-point decreases about 6 times faster than that at the $L$-point due to the SOI.
Figure 3. Low energy band structures for $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ with (left) and without (right) the SOI obtained by the VCA.

Figure 4. Equal energy surfaces for PbTe (left, $\Delta E_F = 126\text{meV}$) and SnTe (right, $\Delta E_F = 228\text{meV}$).

3. Fermi surfaces
Figure 4 shows the equal energy surfaces of PbTe and SnTe. This equal energy surfaces should correspond to the Fermi surfaces of the doped PbTe and SnTe. We have also calculated the Fermi surface of Tl doped PbTe on the basis of the VCA, and have checked the equal energy
surface corresponds to the doped Fermi surface as far as the Tl content is less than 1%

In the case of PbTe, the equal energy surface at the L-point grows as decreasing the energy (doping) for $\Delta E_F < 100$ meV. The shape of the equal energy surface at the L-point is not simply ellipsoidal, but is like a “barrel” [18]. Then, a second pocket appears at around the $\Sigma_0$-point for $\Delta E_F \geq 100$ meV. The shape of the second pocket is almost ellipsoidal but warped as is shown in the left panel of Fig. 2. Both the first and second pocket grow by lowering the energy, and they are connected with each other for $\Delta E_F \geq 140$ meV. The energy region where the second pocket exists is $100$ meV < $\Delta E_F < 140$ meV.

In the case of SnTe, on the other hand, the equal energy surface at the L-point grows solely until $\Delta E_F < 200$ meV. The shape of the first pocket is similar to that of PbTe. Then, the second pocket appears at around $\Delta E_F \approx 200$ meV, but is soon connected to the first pocket as is shown in the right panel of Fig. 2. The energy region where the second pocket is not connected to the first one is only $200$ meV < $\Delta E_F < 210$ meV. Therefore, the doping region where the second pocket exists is very narrow, suggesting that the second pocket is hard to observe practically for SnTe.

4. Conclusion

In the present work the low energy band structures of PbTe and SnTe have been investigated by ab initio calculations. The first-principles calculations within the GGA have been carried out by using the OpenMX code. The tight-binding model has been derived based on the most localized Wannier functions obtained by the first-principles calculations. The direct energy gaps at the L-point have been evaluated to be $\Delta_{Pb} = 0.115$ eV and $\Delta_{Sn} = 0.280$ eV, which are close to those obtained by experiments. There are maxima of the highest valence band near the midpoint ($\Sigma_0$) of the Γ-K line both for PbTe and SnTe. The energy differences between the L- and $\Sigma_0$-points are $E_L - E_{\Sigma_0} = 201$ meV for SnTe and $E_L - E_{\Sigma_0} = 104$ meV for PbTe. This difference between PbTe and SnTe is mainly due to the SOI and brings the topological difference in the Fermi surfaces of doped PbTe and SnTe. For doped PbTe, the second pocket appears at around the $\Sigma_0$-point for wide doping levels. On the other hand, for SnTe, the doping level where the second pocket appears is very narrow, suggesting that the second pocket is hard to observe practically for SnTe.

References

[1] Mahan G D 1997 Good thermoelectrics SOLID STATE PHYSICS vol 51 (ACADEMIC PRESS INC.) p 81
[2] Doiron-Leyraud N 2011 La Physique au Canada 67 89
[3] Hulm J 1969 Phys. Rev. 169 388
[4] Erickson A S, Chu J H, Toney M F, Geballe T H and Fisher I R 2009 Phys. Rev. B 79 024520
[5] Nakayama K, Sato T, Takahashi T and Murakami H 2008 Physical Review Letters 100 227004
[6] Martinez G, Schlüter M and Cohen M L 1975 Phys. Rev. B 11(2) 651–659
[7] Singh D 2010 Phys. Rev. B 81 195217
[8] Littlewood P B, Mihaila B and Schulze R K 2010 Phys. Rev. Lett. 105 086404
[9] Lent C S, Bowen M A, Dow J D, Allgaier R S, Sanky O F and Ho E S 1986 Superlattices Microstruct. 2 491–499
[10] Mitchell D L, Palik E D and Zemel J N 1964 Proc. Seventh Int. Conf. Phys. Semicond. p 325
[11] Dimmock J O, Melngailis I and Strauss A J 1966 Phys. Rev. Lett. 16 1193
[12] Ozaki T 2003 Phys. Rev. B 67 155108
[13] Ozaki T, Kino H, Yu J and Han M J 2014 Openmx package URL http://www.openmx-square.org
[14] Weng H, Ozaki T and Terakura K 2009 Phys. Rev. B 79 235118
[15] Fuseya Y, Ogata M and Fukuyama H 2014 J. Phys. Soc. Jpn. 83 074702.
[16] Fuseya Y, Ogata M and Fukuyama H 2015 J. Phys. Soc. Jpn. 84 012001
[17] Niu C, Dai Y, Ma Y, Yu L and Huang B 2013 Materials Express 3 159
[18] Buchauer L F 2014 Master’s thesis Technische Universität Darmstadt