Spin texture of the surface state of three-dimensional Dirac material Ca₃PbO

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Abstract. The bulk and surface electronic structures of a candidate three-dimensional Dirac material Ca₃PbO and its family are discussed especially focusing on the spin texture on the surface states. We first explain the basic features of the bulk band structure of Ca₃PbO, such as emergence of Dirac fermions near the Fermi energy, and compare it with the other known three-dimensional Dirac semimetals. Then, the surface bands and spin-texture on them are investigated in detail. It is shown that the surface bands exhibit strong momentum–spin locking, which may be useful in some application for spin manipulation, induced by a combination of the inversion symmetry breaking at the surface and the strong spin-orbit coupling of Pb atoms. The surface band structure and the spin-textures are sensitive to the surface types.

1. Introduction
Recently, materials having three-dimensional linear dispersion near the Fermi energy attract much attention [1, 2, 3, 4, 5, 6] as a natural extension of graphene, typical two-dimensional material with linear dispersion near the Fermi energy. Such 3D materials are dubbed as 3D Dirac/Weyl semimetals depending on the degeneracy at the center of the linear dispersion, a Weyl node or a Dirac point. Low-energy physics in the Weyl semimetal is governed by a two-component Weyl equation, and there is two-fold degeneracy at the Weyl node. On the other hand a four-component Dirac equation dominates the low-energy physics in the Dirac semimetal, and we observe a four-fold degeneracy at the Dirac point. Weyl nodes and Dirac points are singularity of the band structure in momentum space. In general, such a singularity in the band structure leads to characteristic surface/edge states [7, 8, 9], for instance, as the edge mode in graphene ribbons. Surface/edge band structures depend crucially on how the Weyl nodes or the Dirac points are projected on the surface Brillouin zone [1].

In this paper, surface states of Ca₃PbO series are studied in detail, especially focusing on the spin texture on the surface bands. Ca₃PbO and its family, such as Ca₃SnO, Sr₃PbO, and Ba₃PbO, were first synthesized back in 1980 [10], and they are theoretically proposed as candidate materials having the 3D Dirac fermion with a tiny mass gap exactly at the Fermi energy [11]. Furthermore, it is also theoretically suggested that Ca₃PbO series is a potential topological crystalline insulator [12]. Then, further study on this series of material is highly demanded. In the following, we first give a brief review on the electronic structure of Ca₃PbO series. There, we explain the bulk band structure obtained by means of the first-principles calculation, and the surface states obtained using a low-energy effective model. In the review part, we also give some up-to-date arguments on 3D Dirac materials, for instance, comparison...
between \( \text{Ca}_3\text{PbO} \) series and other Dirac semimetals, \( \text{Cd}_3\text{As}_2 \) [4] and \( \text{Na}_3\text{Bi} \) [3], which are recognized as Dirac materials very recently. The review part is followed by new results on the spin texture of the surface bands of \( \text{Ca}_3\text{PbO} \).

2. Electronic structure of \( \text{Ca}_3\text{PbO} \) and its family

\( \text{Ca}_3\text{PbO} \) and its family are cubic inverse perovskite materials, in which the metallic atoms, alkaline-earth metals in this case, octahedrally surround the oxygen atom. Experimentally, they are synthesized in 1980, and their lattice constants are reported at that time [10]. Because of the simple crystal structure, only a single parameter, the lattice constant, thoroughly determines the crystal structure.

The electronic structure of \( \text{Ca}_3\text{PbO} \) series was investigated by means of the first-principles calculation with the spin-orbit coupling using the experimental crystal parameters [11]. Close to the Fermi energy, there are almost completely filled Pb-6p orbital originated bands and almost empty Ca-3d bands. However, it is not a simple semiconductor with the closed Pb-6p shell. Instead, if we carefully examine the orbital character of each band, the top of Pb-6p band is above the bottom of Ca-3d bands. Basically, owing to the strong hybridization between Pb-6p and Ca-3d orbitals, Pb-6p and Ca-3d bands strongly repel each other and the gap is formed at the Fermi energy. However, restriction by the crystalline symmetry does not allow strong repulsion between Pb-6p and Ca-3d bands on the \( k_x, k_y, \) and \( k_z \) axis in the Brillouin zone, and the band crossing remains on these axis. Near the band crossing point, i.e., Dirac point, at which the Pb-6p and Ca-3d bands are degenerate, the band gap grows linearly as a function of the distance from the Dirac point in all three directions. This indicates that this material can be regarded as a 3D Dirac material. In short, the orbital overlapping and the protection of the band crossing by the crystalline symmetry play crucial roles in generating Dirac fermions. Strictly speaking, there is a tiny mass gap at the Dirac point induced by the indirect spin-orbit coupling [13]. Here, the indirect spin-orbit coupling means that it should involve orbitals fairly away from the Fermi energy, such as the Pb-5d orbitals. This indirect nature limits the size of the mass gap, and the smallness of the mass gap is guaranteed. Since the mass gap is very small, the linear dispersion, which is crucial in observing interesting phenomena associated with the Dirac fermions, is clearly identified in the band structure.

Here, we make a comparison between \( \text{Ca}_3\text{PbO} \) series and other Dirac semimetals, \( \text{Cd}_3\text{As}_2 \) [4] and \( \text{Na}_3\text{Bi} \) [3]. In \( \text{Cd}_3\text{As}_2 \), Cd-3d orbital originated bands and As-4p bands overlap near the Fermi energy. Similarly, in \( \text{Na}_3\text{Bi} \), Bi-6p bands and Na-3s bands overlap in the vicinity of the Fermi energy. For both of \( \text{Cd}_3\text{As}_2 \) and \( \text{Na}_3\text{Bi} \), the origin of the Dirac point is ascribed to the overlapping of orbitals with different characters and the crystalline symmetry protecting the band crossing, just as in the case of \( \text{Ca}_3\text{PbO} \). However, it should be noted that p- and s-orbitals are involved in \( \text{Cd}_3\text{As}_2 \) or \( \text{Na}_3\text{Bi} \) while p- and d-orbitals are involved in \( \text{Ca}_3\text{PbO} \). The difference between s- and d-orbitals is important in some sense, because the d-orbital contribution is essential for inducing a small but finite mass term in \( \text{Ca}_3\text{PbO} \) [13].

The surface states of \( \text{Ca}_3\text{PbO} \) was also theoretically studied in brief using a low-energy effective tight-binding model [13]. It was shown that there appear characteristic surface states, and the surface band structure is sensitive to the surface direction and termination. Because of the strong spin-orbit coupling served by Pb atoms, the spin texture on the surface bands is an interesting topic to study. However, the spin texture on the surface bands was not studied in detail in the previous work, and the latter half of this paper is devoted to this issue. Revealing the spin texture is also important in terms of application, such as the possible spin manipulation.

Before moving on to the next issue, we point out the other aspect of \( \text{Ca}_3\text{PbO} \). So far, \( \text{Ca}_3\text{PbO} \) is regraded as a Dirac material because the gap is very small. However, strictly speaking, it is an insulator with a small but finite mass gap as we have noted. Very recently, it is proposed that \( \text{Ca}_3\text{PbO} \) is not a mere ordinary insulator, but is a topological crystalline insulator protected
by the reflection symmetry [12]. Then, we can give a topological origin to the surface states discussed above, at least for the surface respecting the reflection symmetry.

3. Spin-texture on the surface states

Let us move on to the spin texture on the surface states of Ca$_3$PbO. For simplicity and clarity, the surface states and the spin texture on them are calculated using the low-energy effective tight-binding model introduced in Ref. [13]. The model is a 12 band (= 2 spins $\times$ 6 orbitals) model, where the six orbitals come from three Pb-6p orbitals and three Ca-3d orbitals. (See Ref. [13] for details.) There are 15 Ca-3d orbitals in a unit cell since three Ca atoms are contained in a unit cell, but only three of them are necessary to reproduce the low-energy band structure. The spin-orbit coupling is taken account of as the atomic $L \cdot S$ coupling on the Pb-6p orbitals, and the $L \cdot S$ coupling on the Ca-3d orbitals are neglected. The surface band structure is calculated using the system with the finite thickness slab geometry. We consider several kinds of surfaces with different surface directions and different terminations. For simplicity, we only treat terminations having perfectly flat surfaces. Further, we focus on the cases where the top and bottom surfaces of the slab are of the same sort of termination.

Let us begin with 001 surfaces. For the 001 surfaces, there exist two possible terminations leading to the flat surfaces, which are illustrated as Figs. 1(b) and 1(c). We call the surfaces in Fig. 1(b) and Fig. 1(c) as 001A and 001B respectively. The surface band structures for these surfaces are plotted in Figs. 1(d) and 1(e). The region filled with bands is a bulk continuum, which is contributed by the bulk part of the system. For both of 001A and 001B surfaces, we observe in-gap surface bands apart from the bulk continuum. Since introduction of 001A or 001B surfaces preserves the reflection symmetry that makes Ca$_3$PbO a topological crystalline insulator, these surface bands have a topological origin [12]. For both of the 001A and 001B surfaces, two surface bands are identified on the $\bar{\Gamma}$-$\bar{X}$ line, while only one surface band is identified on the $\bar{\Gamma}$-$\bar{M}$ line. [See Fig. 1(a) for names of the special points in the surface Brillouin zone.] That is, one of the two surface bands on the $\bar{\Gamma}$-$\bar{X}$ line is absorbed into the bulk continuum as we move from the $\bar{\Gamma}$-$\bar{X}$ line to the $\bar{\Gamma}$-$\bar{M}$ line. The existence of the surface states itself looks robust for the 001 surfaces, but the surface band structure is sensitive to the surface termination. For instance, the slope of the surface bands are opposite between the 001A and 001B surfaces.

The obtained surface bands are doubly degenerate, but this degeneracy is originated from the equivalence of the top and bottom surfaces of the slab. When each surface is examined separately, the surface bands are nondegenerate, i.e., they have no spin degeneracy. This is because there is strong spin-orbit coupling in this system, and the inversion symmetry is broken at the surface. In order to see this point more in detail, we calculate the band and momentum resolved spin moment on the atoms in the outermost layer of the slab. For the 001A surface, there are both of the Pb and Ca atoms at the surface [Fig. 1(b)], and both atoms contribute to the spin moment. On the other hand, for the 001B surface, only the Ca atoms appear at the surface [Fig. 1(c)], and the spin moment contains the contribution from Ca atoms only. (Recall that the O atoms are not included in the effective tight-binding model.)

The calculated spin textures are shown in Figs. 1(f)–1(i). Since we found at most two surface bands, the spin textures are calculated for two bands for each of 001A and 001B surface. Namely, Figs. 1(f) and 1(h) are for the lower surface bands, and Figs. 1(g) and 1(i) are for the upper ones. However, note that some part of the selected bands is merged into the bulk continuum as we have discussed. For instance, only a lower (upper) band among the two selected bands is an in-gap state on the $\bar{\Gamma}$-$\bar{M}$ line for 001A (001B) surface. In Figs. 1(f)–1(i), the spin moment parallel to the surface is expressed by arrows, and the one perpendicular to the surface is represented by the color map. For all the surface bands, the spin textures such that the spin moment winds around the $\bar{\Gamma}$-point are observed. More specifically, the spin moment directs along the isoenergy lines of the surface bands. This momentum-spin locking is caused by a induced Rashba term. Although
we have not added a Rashba term to the Hamiltonian, it is naturally induced by a combination of the inversion symmetry breaking and the bulk atomic $L \cdot S$ coupling. For the 001B surface, only Ca sites, where the atomic $L \cdot S$ coupling are neglected, appear at the surface and contribute to the surface spin moment, but the hybridization between Pb and Ca orbitals induce Rashba effect on Ca sites. Comparing Figs. 1(f)–1(i), we notice that the directions of winding of the spin moment are opposite between the lower and the upper surface bands. Another feature of the spin texture for the 001 surfaces is that there is no spin moment perpendicular to the surface. Figures 1(f)–1(i) also indicate that the spin textures are more clearly seen on the lower (upper) bands for the 001A (001B) surface than the other. This is natural because the upper (lower) bands for the 001A (001B) surface is merged into the bulk continuum. That is, first of all, the momentum-spin locking is caused by inversion symmetry breaking at the surface, and the effect of the inversion symmetry breaking at the surface is smeared and becomes less important if the band gains the bulk character as it is merged to the bulk continuum.

Next, we look at the 111 surface. For the 111 surfaces, there exist two possible flat terminations, but one of them contains only O atoms, which is not included in the low-energy effective tight binding model, at the outermost layer of the surface. Thus, we consider only one type of surface. (See Ref. [13].) As we can see from Fig. 2(b), there appear four surface bands apart from the bulk continuum. Two of the four surface bands, uppermost and lowermost ones form roughly conical band structure and are nearly isotropic in the surface Brillouin zone. On the other hand, middle two surface bands have strong anisotropy. That is, on the $\Gamma$-M line, they are approximately flat, while on the $\Gamma$-X line, they are dispersive. [See Fig. 2(a) for the names of the special points in the surface Brillouin zone.] This anisotropy is related to the projected Dirac points located on the $\Gamma$-M line. The spin textures on these four surface bands are summarized.
Figure 2. (a) Two-dimensional surface Brillouin zone for the 111 surface. Blue dots represent the projected Dirac points. (b) Surface band structure on the high symmetry line in the surface Brillouin zone. (See also Ref. [13].) (c)–(f) Spin texture on the surface bands for the 111 surface. In Figs. 2(c)–2(f). Just as in the case of the 001 surface, we can see a winding structure of the spin moment, which is caused by the induced Rashba term. In contrast to the 001 surfaces, the spin moment normal to the surface is sizable especially for the middle two surface bands. Similar to the surface states of Bi$_2$Te$_3$, a representative time reversal invariant $Z_2$ topological insulator, the hexagonal warping of the surface bands induces the spin moment perpendicular to the surface [14]. Since the uppermost and lowermost surface bands have weak anisotropy, the spin moment perpendicular to the surface is negligible for these bands.

4. Summary
To summarize, we have reviewed the electronic structure of Ca$_3$PbO series, and investigated the spin texture on the surface bands. It is shown that the surface bands exhibit strong momentum–spin locking induced by a combination of the inversion symmetry breaking at the surface and the strong spin-orbit coupling given by Pb atoms. The surface band structure and the spin textures on them sensitively depend on the surface direction and also on the types of the termination at the surface. An interesting future work is to consider the possible application of these surface bands with the unique spin texture. Furthermore, it is also important to think about what kinds of termination are available in experiments.

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