Three-Dimensional Dirac Electrons at the Fermi Energy in Cubic Inverse Perovskites: Ca$_3$PbO and Its Family

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Abstract

The band structure of cubic inverse perovskites, Ca$_3$PbO and its family, are investigated with the first-principles method. A close observation of the band structure reveals that six equivalent Dirac electrons with a very small mass exist on the line connecting the Γ- and X-points, and at the symmetrically equivalent points in the Brillouin zone. The discovered Dirac electrons are three-dimensional and remarkably located exactly at the Fermi energy. A tight-binding model describing the low-energy band structure is also constructed and used to discuss the origin of the Dirac electrons in this material. Materials related to Ca$_3$PbO are also studied, and some design principles for the Dirac electrons in this series of materials are proposed.

KEYWORDS: Dirac electron, inverse perovskite, the first-principles calculation, tight-binding model

"Emergence" is one of the most important concepts in condensed matter physics. Although this key word often appears in the context of many-body or strong correlation effects, emergent behaviors are also observed in noninteracting systems where the low-energy effective Hamiltonian becomes quite distinct from the original Hamiltonian. The most well-known example is the relativistic Dirac Hamiltonian realized in graphene derived from a nonrelativistic Hamiltonian. Many intriguing properties of graphene can be ascribed to the existence of “Dirac electrons” in its low-energy band structure. Actually, Dirac electrons in materials have a long history starting from bismuth, which has three-dimensional massive Dirac electrons in its band structure. The organic conductor $\alpha$-(BETT-TTF)$_2$I$_3$ is also known to be a material having Dirac electrons near the Fermi energy. The most up-to-date example is a surface state of a three-dimensional topological insulator, which is extensively studied in these days.

In connection with topological insulators, inverse-perovskite materials have attracted much attention recently. For example, it is claimed that Ca$_3$NBi enters a topological phase under an appropriate strain engineering scheme. In this paper, we show that cubic inverse perovskites, Ca$_3$PbO and its family, have three-dimensional Dirac electrons with a very small mass at the Fermi energy. Although Ca$_3$PbO is on the list of potential topological insulators proposed by Klintenberg, our close observation of its band structure reveals the existence of bulk (not surface) Dirac electrons on the line connecting the Γ- and X-points, and at the symmetrically equivalent points in the Brillouin zone. Although some first-principles calculations on this material are available in the literature, it is the first time that the existence of Dirac electrons is pointed out. We also construct a tight-binding model that describes the low-energy band structure, and clarify the origin of the Dirac electrons in this material by analyzing the model. We also study the family of Ca$_3$PbO, and some design principles for Dirac electrons in this series of materials are proposed on the basis of the obtained results.

The crystal structure of Ca$_3$PbO is shown in Fig. 1(a). It belongs to the space group $Pm\bar{3}m$ and is an inverse perovskite that possesses an O atom surrounded octahedrally by Ca atoms. Figure 1(b) shows the band structure of Ca$_3$PbO obtained within the first-principles calculation using the WIEN2k package, in which the full-potential augmented-plane-wave method is implemented. The spin-orbit coupling is taken account of within the muffin-tin sphere of each atom via the second variational step. The required crystal parameters are taken from experimental results. $20 \times 20 \times 20$ $k$-points, which result in 220 $k$-points in the reduced Brillouin zone, are employed in the self-consistent cycle of our calculations. The charge density obtained with this number of $k$-points is used to calculate band structures on the finer momentum meshes required to confirm the existence of Dirac electrons. An overview of the calculated band structure shown in Fig. 1(b) is as follows. First, the band at approximately $-8$ eV and the bands between $-4$ and $0$ eV mainly originate from Pb 6s and Pb 6p orbitals, respectively. On the other hand, the bands between $-6$ and

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Fig. 1. (Color online) (a) Cubic inverse-perovskite structure of Ca$_3$PbO. (b) The calculated band structure of Ca$_3$PbO along the high symmetry lines in the Brillouin zone. The location of one of the Dirac points is marked with an arrow.
three orbitals. Based on these results, we use the 12 local orbitals

$$|p_x\sigma\rangle, |p_y\sigma\rangle, |p_z\sigma\rangle, |d_1\sigma\rangle, |d_2\sigma\rangle, |d_3\sigma\rangle, \quad (1)$$

($$\sigma = \uparrow, \downarrow$$) as a basis set for our tight-binding model, where $$d_1$$, $$d_2$$, and $$d_3$$ represent the above-mentioned $$d$$-orbitals on the Ca1, Ca2, and Ca3 sites, respectively. Assuming the nearest-neighbor and next-nearest-neighbor hoppings shown in Fig. 3(b), we have the tight-binding Hamiltonian

$$\hat{H} = \sum_{\sigma} \sum_{\mathbf{r} \mathbf{\rho}} \epsilon_\sigma \hat{c}_\mathbf{\rho}^\dagger \hat{c}_\mathbf{\rho} + \sum_{\sigma} \sum_{\mathbf{r} \mathbf{r}' \mathbf{\sigma}'} t_{\mathbf{\sigma} \mathbf{\sigma}'}^{\mathbf{\rho} \mathbf{\rho}'} (\mathbf{r} - \mathbf{r}') \hat{c}_\mathbf{\rho}^\dagger \hat{c}_{\mathbf{r}' \mathbf{\sigma}'}, \quad (2)$$

where indices $$\mathbf{a}$$ and $$\mathbf{a}'$$ represent $$p_x, y, z$$ or $$d_{1, 2, 3}$$, and the fourth term represents the spin-orbit coupling for Pb atoms. Owing to the Pb $$p$$-orbital character, $$|p_x \uparrow\rangle, |p_y \uparrow\rangle,$$ and $$|p_z \downarrow\rangle$$ are mixed. Here the spin-orbit couplings for Ca atoms are neglected for simplicity. The Fourier transformation of eq. (2) gives

$$\hat{H} = \sum_{\mathbf{k}} \sum_{\alpha \alpha'} \mathcal{E}_{\alpha \alpha'}(\mathbf{k}) \hat{c}_\mathbf{k}^\dagger \hat{c}_{\mathbf{k} \alpha'}. \quad (3)$$

After carrying out the Fourier transformation, we transform the matrix elements by attaching the momentum-dependent phase factors to the basis orbitals as

$$|p_{x, y, z}\sigma\rangle \rightarrow e^{i(k_x x + k_y y + k_z z)/\lambda} |p_{x, y, z}\sigma\rangle, |d_1\sigma\rangle \rightarrow e^{ik_z/2} |d_1\sigma\rangle, |d_2\sigma\rangle \rightarrow e^{ik_y/2} |d_2\sigma\rangle, |d_3\sigma\rangle \rightarrow e^{i(k_x + k_y)/2} d_3\sigma\rangle.$$ This transformation makes the expressions for the matrix elements simple, and the transformed basis and matrix elements are used in the following.

Figure 4(a) shows the band structure of our tight-binding model obtained using the parameter set $$\epsilon_p = -1.25, \lambda p_1 = 0.20, \lambda p_2 = 0.12, \lambda p_3 = 0.06, \lambda d_1 = 2.15, \lambda d_6 = 0.48, \lambda d_4 = 0.22, \lambda d_5 = -0.22, \lambda d_p = 0.22,$$ and $$\lambda = 0.4$$ (in units of eV). Although there are some differences between the first-principles bands and the tight-binding bands, the latter bands reproduce the important features (including the Dirac electrons) of the former bands having large $$d_{1g}$$, $$d_{2g}$$, $$d_{3g}$$, and $$d_{4g}$$ orbital weights. In this simplified model, however, there is no gap at the Dirac point, i.e., we obtain massless Dirac electrons. It is necessary to include Ca $$d_{xy}$$ or $$d_{xz/yz}$$ orbitals to have a finite mass term. (Details will be published elsewhere.)
In order to obtain a clearer view on the emergence of the Dirac electrons, we derive a low-energy effective Hamiltonian of the above tight-binding model and show that it really results in a Dirac Hamiltonian. Firstly, by introducing a new basis set, we eliminate the uppermost and lowermost bands, which are well separated from the bands forming Dirac electrons. Since the Dirac point is close to the Γ-point, we use the new basis set, which consists of the eigenstates at the Γ-point. At the Γ-point, we can treat the p- and d-orbitals separately since the hybridization between them becomes zero. For the p-orbitals, the eigenvalues are $\epsilon_p + \lambda$ and $\epsilon_p - 2\lambda$, where $\epsilon_p \equiv \epsilon_p + 2t_{p1} + 4t_{p2} + 4t_{p3}$ We find that the former corresponds to the states forming the Dirac electrons and the latter to the lowermost band. The energy splitting between them is caused by the spin-orbit coupling, and the former has a total angular momentum of $j = 3/2$.

The new basis set for $j = 3/2$ states is

\[ |\tilde{p}^{\pm}_{\pm}\rangle = (-|p^\uparrow\rangle + i|p^\downarrow\rangle)/\sqrt{2}, \]

\[ |\tilde{p}^+_{\pm}\rangle = (-|p^\uparrow\rangle + i|p^\downarrow\rangle - 2|p^\uparrow\rangle)/\sqrt{6}, \]

\[ |\tilde{p}^+_{\mp}\rangle = (|p^\uparrow\rangle - i|p^\downarrow\rangle + 2|p^\downarrow\rangle)/\sqrt{6}, \]

\[ |\tilde{p}^0_{\pm}\rangle = (|p^\downarrow\rangle - i|p^\uparrow\rangle)/\sqrt{2}. \]

For the d-orbitals, the eigenvalues are $\epsilon_{d0} - 4t_{d0}$ and $\epsilon_{d0} + 4t_{d0}$, where $\epsilon_{d0} \equiv \epsilon_d + 2t_{d1} + 4t_{d2}$. The former corresponds to the bands near the Fermi energy and latter to the uppermost band. Explicitly, the wave functions for the former are

\[ |\tilde{d}_1^\uparrow\rangle = (|d_1\uparrow\rangle - |d_1\downarrow\rangle)/\sqrt{2}, \]

\[ |\tilde{d}_2^\uparrow\rangle = (|d_1\uparrow\rangle + |d_1\downarrow\rangle - 2|d_1\downarrow\rangle)/\sqrt{6}. \]

Performing a unitary transformation from the basis set of eq. (1) into that containing eqs. (4) and (5), we transform the $12 \times 12$ matrix, $\hat{\mathcal{E}}_k$, in eq. (3) into $\hat{\mathcal{E}}_k$. Then, we keep only the matrix elements between the above eight states in eqs. (4) and (5), reducing the matrix $\hat{\mathcal{E}}_k$ into an $8 \times 8$ matrix. Finally, concentrating on the Dirac point on the $k_z$-axis, we expand the matrix elements with respect to $k_x$ and $k_y$ up to the first order in $k_x$ and $k_y$. After some algebra, we obtain

\[
\hat{\mathcal{E}}''_k = \begin{pmatrix}
g_{11}^{pp} & 0 & 0 & -c_1 k_- & c_2 k_+ & 0 & 0 & 0 \\
g_{21}^{pp} & c_3 & 0 & -c_1 k_-' & c_2 k_+' & 0 & 0 & 0 \\
g_{12}^{pp} & 0 & g_{12}^{dd} & 0 & 0 & 0 & 0 & 0 \\
g_{22}^{pp} & 0 & 0 & c_3 k_-' & c_2 k_+' & 0 & 0 & 0 \\
g_{13}^{pp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g_{23}^{pp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g_{14}^{pp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
g_{24}^{pp} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\end{pmatrix},
\]

where $k_\pm = k_x + ik_y$, $c_1' = c_1/\sqrt{3}$, $c_2' = c_2/\sqrt{3}$, and $c_1 = ia_{dp} \cos(k_z/2)$, $c_2 = ia_{dp} (2 + \cos(k_z/2))/\sqrt{3}$, $c_3 = -8it_{dp} \sin(k_z/2)/\sqrt{3}$.

Note that now the new basis set is \{|$p_{x+}$\}, |$p_{x-}$\}, |$p_{y+}$\}, |$p_{y-}$\}, |$d_{1\uparrow}$\}, |$d_{2\uparrow}$\}, |$d_{1\downarrow}$\}, |$d_{2\downarrow}$\}. Note also that $g_{1 \gamma}^{pp}$ and $g_{i \gamma}^{dd}$ depend on $k_z$.

In the limit of $k_x = k_y = 0$, all of the off-diagonal elements in eq. (6) vanish except for the elements represented as $c_3$. The finite $c_3$ induces the strong band repulsion between bands from |$p_{x+}$\rangle and |$d_{1\uparrow}$\rangle (second and fifth rows), and also between bands from |$p_{x-}$\rangle and |$d_{1\downarrow}$\rangle (third and seventh rows). As a result, the bands originating from these states are pushed away from the Fermi energy, and thus we can neglect these states, keeping only |$p_{x+}$\rangle, |$p_{x-}$\rangle, |$d_{2\uparrow}$\rangle, and |$d_{2\downarrow}$\rangle in the following. Then, suppose that $g_{1 \gamma}^{pp} = g_{2 \gamma}^{dd}$ is satisfied at some $k_{z0}$. When $g_{1 \gamma}^{pp} = g_{2 \gamma}^{dd}$ holds, we can expand $g_{1 \gamma}^{pp}$ and $g_{2 \gamma}^{dd}$ as $g_{1 \gamma}^{pp} = -c_0 \delta k_z + e_0$ and $g_{2 \gamma}^{dd} = c_d \delta k_z + e_0$, where $\delta k_z = k_z - k_{z0}$ and $c_0 = g_{11}^{pp} (= g_{22}^{dd})$ at $k_z = k_{z0}$. Using these relations, the Hamiltonian can be written as

\[
\hat{\mathcal{E}}''_k = (\epsilon_0 + \delta c \delta k_z) \hat{1} + \begin{pmatrix}
-c\delta k_z & 0 & c_2 k_+ & 0 \\
0 & 0 & c_2 k_+ & 0 \\
-c\delta k_z & 0 & -c k_-' & 0 \\
0 & 0 & 0 & 0 \\
\end{pmatrix},
\]

with $c = (c_d + c_p)/2$ and $\delta c = (c_d - c_p)/2$, which gives a tilted massless Dirac Hamiltonian. The Dirac point is (0, 0, $k_{z0}$) in this case.

A very simple and intuitive reason for the emergence of the Dirac electrons is obtained from the above analysis. Figure 4(b) shows the energy dispersion of the tight-binding model, where $t_{dp}$ is artificially set to zero. This corresponds to the case that there is no hybridization between the p- and d-orbitals. In this case, the p-bands (d-bands) have a usual hole (electron) Fermi surface around the Γ-point. Although the p- and d-bands overlap with each other, this only leads to a usual band crossing. If we turn on the hybridization $t_{dp}$, it generally causes a band repulsion between the p- and d-bands. However, owing to the symmetry of the involved orbitals, this band repulsion does not act on the Γ-X line. As a result, the band crossing remains at an isolated point in the Brillouin zone, leading to the emergence of a Dirac electron. Note that the existence of an overlap between the p- and d-bands supports the assumption $g_{1 \gamma}^{pp} = g_{2 \gamma}^{dd}$ in the previous paragraph. Thus, we can state that the overlapping between the p- and d-bands is essential for Dirac elec-
trons to appear in this model.

Next, we discuss the reason why the band repulsion does not act on the Γ-X line. On the $k_z$-axis, which is equivalent to the Γ-X line, the $d$-orbital wave function can be classified as shown in Figs. 5(a)-5(c). Actually, $|d' \sigma \rangle$ corresponds to the wave function in Fig. 5(c), while $|d'' \sigma \rangle$ is a superposition of those in Figs. 5(a) and 5(b). From these figures, we can easily see that all of the hybridization between the Pb $p$-orbitals and the wave functions in Fig. 5 vanish except for that between the $p_z$ orbitals and the wave function in Fig. 5(c). This is the reason why we have a finite off-diagonal matrix element $c_3$ for $|d' \sigma \rangle$, while the off-diagonal matrix elements for $|d'' \sigma \rangle$ vanish as $|k| \to 0$. The vanishing matrix elements imply that the band repulsion does not act.

Note that, although the above graphical argument is heuristic and intuitive, the spin-orbit coupling is not taken into account in this argument. By analyzing the irreducible representation of the bands obtained in the first-principles calculation, we find that the two bands forming the Dirac electrons fall into the same irreducible representation on the Γ-X line. As a result, there is a small hybridization between them, leading to a small mass (gap) term. The arguments based on Figs. 5(a)-5(c) give a reason for the smallness of the induced mass gap. If the spin-orbit coupling is neglected, the two bands forming the Dirac electrons belong to different irreducible representations on the Γ-X line, so that a gap does not open. Namely, the spin-orbit coupling is necessary to make the mass term finite, even if $d_{2z}$ or $d_{xy}$ orbitals are included in the tight-binding model.

We discuss some points hereafter. The first is about related materials. We studied the band structures of the family of Ca$_3$PbO, namely, Sr$_3$PbO, Ba$_3$PbO, and Ca$_3$SnO. (Figures are not shown here.) In the calculation, the lattice constants of these materials are again taken from experimental results. We find that all these systems have similar band structures and Dirac electrons. We point out here that the overlap of the $p$- and $d$-bands, which is essential for the existence of Dirac electrons, becomes larger in the order Ca$_3$PbO → Sr$_3$PbO → Ba$_3$PbO. However, in Ba$_3$PbO, some other (non-Dirac) bands appear at the Fermi energy, which may mask the properties of the Dirac electrons. For Ca$_3$SnO, the overlap of the $p$- and $d$-bands becomes smaller than that in Ca$_3$PbO, but it still exists and gives Dirac electrons at the Fermi energy. Since the spin-orbit coupling is smaller for Sn than for Pb, the estimated mass gap is actually as small as 4 meV, compared with 14 meV for Ca$_3$PbO.

From this result, we propose that the series of alloys Ca$_3$(Pb$_{1-x}$Sn$_x$)O will provide a method of controlling the mass term of Dirac electrons.

Compared with Bi, which has three-dimensional massive Dirac electrons in its low energy band structure, the present system has a simple structure whose Fermi energy is located in the gap of the Dirac electrons. In Bi, on the other hand, there is a complication due to its semimetallic properties. As a result, fine-tuning of the doping or pressure is necessary for studying the Dirac electrons in Bi. Ca$_3$PbO and its family will be interesting and important materials for exploring the three-dimensional Dirac electrons.

Responses to applied magnetic fields will also be interesting. Neglecting the small gap, a Dirac electron has a linear dispersion, leading to a peculiar Landau level structure. Another possible interesting response is a large orbital diamagnetism, which is observed in Bi. The orbital diamagnetism takes a maximum when the Fermi energy is inside the gap, namely, a large electronic response is observed even though there are no Fermi surfaces. The interesting interband effects in the quantum transport phenomenon are being extensively studied.

If a small number of electrons (or holes) are doped to this material, it becomes a metal with six tiny Fermi surfaces, or six valleys. It will be interesting to consider the possibility of a three-dimensional analogue of valleytronics, which has recently been developed for graphene.

It is also interesting to consider the possibility of spontaneous valley symmetry breaking, in which the occupancy of the valleys spontaneously becomes imbalanced.

In summary, we have performed the band structure calculation of Ca$_3$PbO and its family, and found that three-dimensional massive Dirac electrons exist at the Fermi energy. A tight-binding model that describes the essence of the emergence of Dirac electrons was successfully constructed. By analyzing this model, it is concluded that the symmetry of the crystal and the involved orbitals play important roles in sustaining Dirac electrons in the band structure.

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