Weyl Ferroelectric Semimetal

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The recent discoveries of ferroelectric metal and Weyl semimetal (WSM) have stimulated a natural question: whether these two exotic states of matter can coexist in a single material or not. These two discoveries ensure us that physically it is possible since both of them share the same necessary condition, the broken inversion symmetry. Here, by using first-principles calculations, we demonstrate that the experimentally synthesized nonmagnetic HgPbO₃ represents a unique example of such hybrid “Weyl ferroelectric semimetal”. Its centrosymmetric R₃c phase will undergo a ferroelectric phase transition to the ferroelectric R₃c structure. Both phases are metallic and the ferroelectric phase owns a spontaneous polarization of 33 mC/cm². Most importantly, it also harbors six pairs of chiral Weyl nodes around the Fermi level to be an oxide WSM. The structural symmetry broken phase transition induces a topological phase transition. The coexistence of ferroelectricity and Weyl nodes in HgPbO₃ is an ideal platform for exploring multiphase interaction and mutual control. The Weyl nodes can be tuned by external pulse electric field, which is promising for potential applications of integrated topotronic and ferroelectric devices.

I. INTRODUCTION

Noncentrosymmetric (NCS) lattice is an important asset for hosting two seemingly incompatible phenomena: ferroelectricity and topological semimetals, such as WSM. Ferroelectricity arises from the formation of electric dipoles due to the separated centers of positive and negative charges under polar distortion, as shown in Fig. I(a). Owing to the screening of free carriers in metals, ferroelectricity and ferroelectric phase transition are generally thought to occur only in insulators. However, in 1965 P. W. Anderson and E. I. Blount suggested that, if a structural transition occurs in a metal that is accompanied by the appearance of a polar axis and the disappearance of inversion center, a “ferroelectric metal” can be expected. Indeed, ferroelectric metallic state and the ferroelectric phase transition have been recently discovered in LiOsO₃-5 and several other oxides.6-5. On the other hand, NCS WSM with time reversal symmetry have also been discovered.6-8 The lack of inversion center breaks the Kramer degeneracy, leading to separation of chiral Weyl nodes, which are formed by crossing of two non-degenerate bands around Fermi level. Within this context, in principle the ferroelectricity and WSMs can coexist in a single material.

Although several nonmagnetic WSMs, such as TaAs family,9-12 Ta₃S₈,13 TaIrTe,14 WTe₂,15-16 chemically doped KMgB₁₀,20-22 chalcopyrites like Cu₂TlSe,23,27 HgTe class materials,18 and ZrTe₂ have been proposed and partially experimentally confirmed, neither ferroelectricity nor ferroelectric phase transition has been reported. According to the space group of these crystals, the former five materials can have ferroelectricity because the electric dipole is allowed to exist, whereas the latter three cases are expected to have piezoelectricity due to the nonexistence of polar axis. The ferroelectric phase transition is accompanied with the inversion symmetry breaking and, hence, it is also possible to induce topological phase transition to WSM since the inversion symmetry and time reversal symmetry result in Kramer degeneracy in bands and prevent the separation of Weyl nodes with opposite chirality.

To form ferroelectric metal it is necessary to have a finite occupation at the Fermi level and an electronic structure insensitive to polar ionic displacement in a polar lattice,1-5, thus ensuring that orbital-like electronic states at the Fermi level are decoupled from the polar displacement. On the other hand, the design principles for WSMs include a fully filled band at the border of a semiconducting regime and a strong spin-orbit coupling (SOC) which could cause large Rashba-like spin splitting in a NCS lattice. By combining these design principles we achieve the following criteria for the realization of coexisting Weyl nodes and ferroelectric metal: (i) a polar and flexible lattice, (ii) fully filled electron orbitals, and (iii) strong SOC. Clearly, oxides represent the most promising playground owing to their chemical and structural flexibility and to the abundance of data available in literature.25,26 To fulfill the fully-filled orbital condition we adopted the simple chemical concept of electronegativity as used in our previous work.27 Finally, the strength of SOC can be estimated from the atomic number of the atomic constituents. We find that these conditions are simultaneously satisfied in the rhombohedral oxide HgPbO₃. Based on first-principles calculation we demonstrate that HgPbO₃ is a WSM with ferroelectric phase transition, that we name “Weyl ferroelectric semimetal”. 

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II. COMPUTATIONAL METHODS

1) Structural optimizations and electronic band structures The structural optimization and electronic properties were performed within the framework of the density functional theory (DFT) based on the Vienna ab initio simulation package (VASP) based on the projector augmented wave (PAW) method. We have used the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE). The adopted PAW-PBE pseudopotentials of Hg, Pb and O treat 5d106s1, 5d106s26p2 and 2s22p3 electrons as valence states. The energy cutoff was set at 500 eV and appropriate Monkhorst-Pack k meshes (13×13×13) were chosen. A very accurate criteria were used for the structural relaxation (forces < 0.0001 eV/Å). In order to double check the electronic band structures with the presence of Dirac and Weyl nodes, we have also employed the hybrid density functional theory developed by Heyd, Scuseria and Ernzerhof (HSE) and the GW method. For HSE, we have adopted the standard set-up for μ and α: μ = 0.20 Å⁻¹ controls the range separation between the short-range and long-range parts of the Coulomb kernel and whereas α = 0.25 is the mixing parameter determining the fraction of exact Hartree-Fock exchange incorporated.

2) Phonon calculations To inspect the dynamical stability of the ground state structure, we carried out phonon calculations. The phonon properties were computed using finite-displacements and density functional perturbation theory (DFPT), in supercells containing 2×2×2 primitive cells. The phonon spectra was derived by interfacing VASp with the code Phonopy.

3) Surface electronic band structures The surface state calculations have been performed using a Green’s function based tight-binding (TB) approach. The TB model Hamiltonian was constructed by means of maximally-localized Wannier functions (MLWFs) obtained by the the Wannier90 code and constructed from s-, p-, d atomic-like orbitals. The TB parameters were obtained from the MLWFs overlap matrix.

4) Electric polarization calculations The spontaneous electric polarization is estimated by $P_α = \sum_{\mathbf{k},\beta} \langle \mathbf{Z}^v, \mathbf{Hg}: +2; \mathbf{Pb}: +4; \mathbf{O}: -2 \rangle$ and atom displacements (u) of the polar structure (R3c) with respect to the reference phase R3c, where $\omega$ and $e$ are the volume of the unit cell and the elementary electron charge, respectively.

III. RESULTS AND DISCUSSIONS

HgPbO3 was synthesized in 1973 in the temperature range 600-1000 °C under 30 to 65 kbars pressure. Unlike the isostructural CdPbO3 which was found to be a polar semiconductor, HgPbO3 was reported to be black and weakly conducting (ρ ≈ 10⁻³ ohm/cm). Experimental ambiguity on the crystal structure remains, specifically on whether HgPbO3 is polar (R3c) or nonpolar (R3c), see Fig. [1](a). To clarify this issue we have conducted a direct comparison between the two phases and found that the R3c phase is more stable than R3c by 3 meV/atom. Further support for this conclusion is provided by the calculated phonon dispersions. As shown in Fig. [2] the nonpolar R3c phase has imaginary frequencies whereas the polar R3c phase does not have and is dynamically stable.

The most unstable phonon mode of the R3c phase is the infrared active mode of A2g at $\Gamma$ (Γ2), which involves the cooperative displacements of the negatively charged oxygen ions opposite to the positively charged Hg and Pb cations along the c-axis of the hexagonal lattice, or equivalently the <111> direction of rhombohedral lattice, as shown in Fig. [3]. By freezing the $\Gamma_2$ mode at different amplitude, the centrosymmetric R3c lattice is shown to be transformed into the polar R3c lattice with energy gain of 3 meV/atom (Fig. [4]) at the ground state. All of these distorted crystals are metallic in their band structure, reflecting well the experimentally measured weak conductivity. By using the normal charges of cations and anion (Hg: +2; Pb: +4; O: -2), the estimated spontaneous polarization along the polar axis c is as high as 33 μC/cm². The rather small energy change (3 meV/atom) during this process implies an accessible ferroelectric phase transition with decreasing temperature. This is consistent with the analysis of Anderson and Blount for the identification of a ferroelectric metal. Similar to the prototype ferroelectric metal LiOsO3, the main polar distortion arises from opposite displacements of the A-site cation (Hg) (0.37 Å) and O atoms (0.27 Å) along the c-axis. The B-site (Pb) cation has the smallest displacement (0.1 Å). Considering the large polar distortion (0.53 Å in amplitude of $\Gamma_2$ mode), small energy difference $\Delta E$ between the

![Crystal structure and Brillouin zone (BZ) of HgPbO3. Panel (a) denotes the unit cell of centrosymmetric $R3\bar{c}$ rhombohedral lattice. The arrows at each atom denote the atomic displacement in the softest phonon mode $\Gamma_2$ with imaginary frequency of 1.28/THz at $\Gamma$ in Fig. 2. Such polar distortion leads to its ferroelectric phase of $R3c$ lattice. Panel (b) shows the BZ and high symmetrical k-points of the rhombohedral lattice, as well as the projected (111) and (112) surfaces BZ.](image-url)
FIG. 2. Phonons and ferroelectric distortion of HgPbO$_3$. Calculated phonon dispersions for the nonpolar $R\bar{3}c$ (a) and polar $R3c$ (b) structures. (c) The energy difference $\Delta E$ between the polar and nonpolar phases and (d) the electric polarization $P$ as a function of the amplitude ($A_0$, $\ldots$, $A_{11}$) of the frozen polar mode $\Gamma_2$.

FIG. 3. Calculated electronic band structures of HgPbO$_3$. Panels (a) and (b) are those calculated without SOC for the nonpolar $R\bar{3}c$ and polar $R3c$ phases, respectively. Panels (c) and (d) are the corresponding ones with SOC included. The insets stress the crossing (without SOC) and anti-crossing (with SOC) of the bands mainly composed of 6$s$ orbitals of Hg and Pb atoms and 2$p$ orbitals of oxygen atoms.

FIG. 4. Weyl nodes and their distribution in the BZ of the most stable ferroelectric $R3c$ HgPbO$_3$. One of the Weyl node is at $(0.15273470, 0.06175918, -0.01762040)$ and all the others can be obtained by imposing crystal and time-reversal symmetries (see the supplementary Table S1). Panel (a): three-dimensional visualization of the Weyl nodes in the BZ, (b) two-dimensional projection along the $<111>$ direction and the panel (c) is the enlarged plot of the projected Weyl nodes, and (d) two-dimensional projection along the $<11\bar{2}>$ direction and the panel (e) is the enlarged plot of the projected Weyl nodes. The green and blue points denote the opposite chirality of the corresponding nodes. Panel (f) shows the changes in the band structure at one Weyl node as the function of the amplitude of polar distortion ($A_0$, $\ldots$, $A_{11}$ as labeled in Fig. 2c) along the path parallel with the $\Gamma-\bar{K}$.

polar and nonpolar phase, and weak screening in semimetal of low carrier density, the polar ground state is expected to be tunable by applying suitable pulse electric field opposite to the 'spontaneous polarization'.

The inspection of the electronic structures shows that in HgPdO$_3$ the ferroelectric instability is coupled with striking topological phase transition from a normal semimetal to a WSM with Weyl nodes, as evidenced in Figs. 3 and 4. By neglecting the SOC, the band structure of the $R\bar{3}c$ and $R3c$ phases are very similar, characterized by a band crossing around the Fermi level along the $\Gamma-T$ direction. One of the band is a nondegenerate band mainly composed of 6$s$ orbitals from Hg and Pb atoms, while the others are double degenerate bands mostly of oxygen atoms’ 2$p$ orbitals. Such $s-p$ band inversion (supplementary Fig. S1) leads to a triply degenerate nodal point along $\Gamma-T$, similar to that in TaN and others.$^{19,29,30}$ However, such triply degenerated nodal point becomes gaped once SOC is further included. In the polar $R3c$ case, the gap is about 7 meV and in the centrosymmetric $R\bar{3}c$ case the gap is smaller, about 5 meV. It needs to be emphasized that electronic structure obtained using the more accurate hybrid functionals (HSE) and GW methods is almost identical to the DFT one (supplemental Fig. S2 and Fig. S3). Another most important difference between these two phases is that the Kramer degeneracy is broken in ferroelectric one. The Rashba like splitting can be clearly seen when compar-
ing the bands around Γ along either Γ-Σ or Γ-L. This might lead to appearance of separated chiral Weyl nodes in NCS polar R3c phase. And indeed, we have identified that there are totally six pairs of Weyl nodes in the first BZ as shown in Fig. 4. Each of them is related with the others by C3 rotational symmetry around the c axis, the mirror symmetries with mirror planes passing through Γ-T and Γ-L, and the time-reversal symmetry. The energy of the Weyl node is around 22 meV below the Fermi level. The exact position and the chirality of these Weyl nodes are specified in supplementary Table S1. The Weyl cone shape can be seen from the energy dispersions along several different directions as shown in supplementary Fig. S4. Again, we monitor the evolution of band structure around one Weyl node as the amplitude of the polar distortion of Γ2 soft mode changes. As clearly shown in Fig. 4, the topological phase transition happens during the ferroelectric phase transition. Thus, we have identified an unusual and tunable coupling between topological Weyl fermion and the ferroelectric properties.

WSM often exhibits nontrivial surface states7,8, such as Fermi arcs. To inspect them for the ferroelectric HgPbO3, we calculate the surface electronic band structures within the tight-binding model based Green’s function method. The Wannier functions are generated from the the bulk Hg 6s, Hg 5d, Pb 6s and O 2p orbitals as the basis set of tight-binding model. Fig. 5 shows the (111) surface band structures and their corresponding Fermi surfaces at the energy of Weyl nodes for the top and bottom surfaces. As illustrated in Fig. 5a and 5b, the projected Weyl nodes are hidden by the other overlapped bulk states. But there are still some surface states with quite high surface local density of states can be identified. Fig. 5c and 5d are the plotting of Fermi surface with chemical potential at Weyl nodes. The Fermi arcs connecting the projection of the Weyl nodes with opposite chirality are well resolved for both top and bottom surfaces. We have also checked the surface electronic bands on the (112) top and bottom surfaces, perpendicular to the (111) surface (see supplementary Fig. S5(a and b)). However, all these projected Weyl nodes on the (112) surface still overlaps the bulk bands as illustrated in supplementary Fig. S5(c and d).

Finally, to reveal the underlying mechanism of the coexistence between WSM and ferroelectricity in HgPbO3, we find that the charges at the Weyl nodes mainly contribute to well localized charge redistribution associated with the formation of local dipole moments, as shown in Fig. 6. It is clear that ferroelectric-like phases are not expected to form in metals, mainly because the screening potential imposed by free electrons in metals prevents the electric dipoles from feeling each other and, hence, stops them from aligning in order26. However, compared to standard metals, WSM appear to be a more
suitable platform to host ferroelectric metal, since the charge carriers in Weyl nodes predominantly move along the linearly dispersive bands forming the nodes. Due to this confinement, Weyl carriers are not expected to be easily redistributed in all the lattice space but localized on the orbitals composing the linear bands. This is different from the nearly free electrons with parabolic band dispersion in normal metals, where the electrons can travel over all the lattice space to be extended. Moreover, the strength of electrostatic screening in WSM is much weaker than the normal metal due to the much lower carrier density. Therefore, if a NCS lattice of WSM is flexible enough to allow the cooperative atomic displacement with the positively and negatively charged ions to form electric dipoles in a proper ferroelectric pattern, this most probably will form a Weyl ferroelectric semimetal.

IV. CONCLUSIONS

In conclusion, we have shown that HgPbO$_3$ is a semimetal with ferroelectric phase transition and its dynamically stable R3c phase has dipole moment. Notably, such ferroelectric metal possesses six pairs of Weyl nodes, which represents the first example of an oxide Weyl ferroelectric semimetal. The Weyl nodes can be selectively tuned by applying an external pulse electric field, implying potential applications as quantum switch in processing devices. The coexistence and the coupling between WSM phase and the ferroelectric phase transition, assisted by strong relativistic effects in a NCS background, has been achieved by judicious material design based on well-defined building criteria. It represents a unique feature never observed hitherto in known Weyl semimetals\cite{14} and ferroelectric metals\cite{15}. This opens the way to novel quantum devices based on topological multifunctional materials.

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TABLE I. Supplementary Table S1: Positions and chirality of six pairs of Weyl nodes in the first Brillouin zone. The position \((k_x, k_y, k_z)\) are in units of reciprocal lattices. All of them are related by crystal and time-reversal symmetries.

| Weyl point | \(k_x\)  | \(k_y\)  | \(k_z\)  | Chirality |
|------------|----------|----------|----------|-----------|
| W1         | 0.15273470 | 0.06175918 | -0.01762040 | -         |
| W2         | 0.01762040  | -0.06175918 | -0.15273470 | +         |
| W3         | -0.01762040 | 0.15273469  | 0.06175918  | -         |
| W4         | -0.15273470 | 0.01762040  | -0.06175918 | +         |
| W5         | 0.01762040  | -0.06175918 | 0.15273469  | -         |
| W6         | -0.01762040 | -0.15273469 | 0.01762040  | -         |
| W7         | -0.15273469 | 0.01762040  | -0.06175918 | +         |
| W8         | -0.01762040 | 0.06175918  | 0.15273469  | +         |
| W9         | 0.01762040  | -0.15273469 | -0.06175180 | -         |
| W10        | 0.15273469  | -0.01762040 | 0.06175918  | -         |
| W11        | -0.06175918 | 0.01762040  | -0.15273469 | +         |
| W12        | 0.06175918  | 0.15273469  | -0.01762040 | -         |

FIG. 7. Supplementary Fig. S1. \(s \rightarrow p\) band inversion. To elucidate band inversion mechanism, we have analyzed the band sequences of the \(R3c\)-type \(\text{HgPbO}_3\) at the equilibrium state (a) in comparison with the artificial state by reducing the volume to 50% of the equilibrium volume. It can be seen that, at the equilibrium state the band structure shows a semimetal, whereas at the reduced volume it becomes an insulator. In the meanwhile, the band inversion occurs between the \(s\)-like orbitals from Hg and Pb atoms and the \(p\)-like orbitals from oxygen atoms.

FIG. 8. Supplementary Fig. S2. HSE derived electronic band structures of \(\text{HgPbO}_3\). Due to the well-known false-positive problem of standard DFT calculations, HSE method with SOC has been performed to check whether the topologically non-trivial states in \(\text{HgPbO}_3\) still exists when a more accurate exchange-correlation functional is introduced. The derived band structure of the NCS \(R3c\) and centrosymmetric \(\bar{R}3c\) structures in (a) and (b), respectively, are very similarity to the DFT calculations.
FIG. 9. Supplementary Fig.S3. **GW derived electronic densities of states (DOSs) of R3c HgPbO_3.** Because HgPbO_3 is semimetal, the GW method is not a most proper method to derive its electronic band structures. However, according to our calculations, the GW method still revealed that the GW DOSs show a clear sign of the semimetal feature, as evidenced by a highly low density at the Fermi level.

FIG. 10. Supplementary Fig.S4. **Calculated band structure along three directions passing through one Weyl node in the polar R3c phase of HgPbO_3.** Panels (a), (b) and (c) are those with k-path parallel to \( \bar{\Gamma}-\bar{K}, \bar{\Gamma}-\bar{M} \) and \( \bar{\Gamma}-\bar{T} \), respectively.
FIG. 11. Supplementary Fig. S5. Calculated (11$\bar{2}$) surface electron structures for the polar R3c phase of HgPbO$_3$. Panels (a) and (b) are the calculated band structures of the top and bottom surfaces, respectively. Panels (c) and (d) are the Fermi surfaces at -22 meV below the Fermi level in panels (a) and (b), respectively. Blue and green points are the surface projections of the Weyl nodes of the opposite chirality.