Predicted Realization of Cubic Dirac Fermion in Quasi-One-Dimensional Transition-Metal Monochalcogenides

Qihang Liu* and Alex Zunger

Renewable Stable Energy Institute, University of Colorado, Boulder, Colorado 80309, USA

(Received 30 November 2016; revised manuscript received 13 February 2017; published 9 May 2017)

We show that the previously predicted "cubic Dirac fermion," composed of six conventional Weyl fermions including three with left-handed and three with right-handed chirality, is realized in a specific, stable solid state system that has been made years ago, but was not appreciated as a "cubically dispersed Dirac semimetal" (CDSM). We identify the crystal symmetry constraints and find the space group $P6_3/mmc$ as one of the two that can support a CDSM, of which the characteristic band crossing has linear dispersion along the principle axis but cubic dispersion in the plane perpendicular to it. We then conduct a material search using density functional theory, identifying a group of quasi-one-dimensional molybdenum monochalcogenide compounds $A^{I}MoX^{VI}$ (A^{I}: Na, K, Rb, In, Tl; X^{VI}: S, Se, Te) as ideal CDSM candidates. Studying the stability of the $AMoX$ family reveals a few candidates such as $RbMoTe$ and $TlMoTe$ that are predicted to be resilient to Peierls distortion, thus retaining the metallic character. Furthermore, the combination of one dimensionality and metallic nature in this family provides a platform for unusual optical signature—polarization-dependent metallic vs insulating response.

DOI: 10.1103/PhysRevX.7.021019

Subject Areas: Condensed Matter Physics, Materials Science

I. INTRODUCTION

The crossing on energy bands in complex materials showing dense manifold of states is a ubiquitous effect routinely reported in the past ~

$$H(\boldsymbol{k}) = \begin{pmatrix} a(\boldsymbol{k})\sigma_z & a_2(\boldsymbol{k})\sigma_y \\ a(\boldsymbol{k})\sigma_x & -ia(\boldsymbol{k})\sigma_z \end{pmatrix}$$

G . G $_0$ bands, and thus, they have {p; q , {2; 0 ,

short-long-short-long bonding with each other. Interestingly, the three Se atoms within the same plane of each Mo triangle tend to move oppositely and thus form a buckled in-plane structure. We applied such a distortion mode to the undistorted structure, and after relaxation, we found that such Peierls distortion indeed eliminates the negative phonon modes [see Fig. 4(c)] as well as lowers the

and Tl MoSe and In MoSe

linear-dispersing direction, the quadratic and cubic-dispersing directions have enhanced density of states near the band-crossing point, which results in stronger screening. Specifically, in CDSM (n), the Coulomb interactions along the in-plane directions are screened with a faster decay than that along the rotation axis (r^{-}). Recently, it was predicted that WSM with n , in the presence of short-range interactions, can easily undergo a continuous quantum phase transition into either a translational symmetry-breaking axion insulator or a rotational symmetry-breaking nematic state [60]. Furthermore, the nonlinear dispersion and the 1D nature of a condensed-matter system would cause a breakdown of the interacting Fermi liquid theory for electron behavior, leading to Luttinger liquid instead.

ACKNOWLEDGEMENTS

We thank Professor L. Fu and Dr. J. Liu for reading this manuscript and making insightful comments. We also thank Professor V. Juricic, Dr. X. Zhang, Dr. M. Hoesch, and Dr. X. Zhou for helpful discussions and codes. This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division under Grant No. DE-SC0010467 to University of Colorado, Boulder. This work used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

APPENDIX A: CLASSIFICATION OF DIFFERENT TYPES OF FERMIONS IN SOLID-STATE PHYSICS

Table II shows examples of materials that host different types of fermions classified by the degree of degeneracy (g) and the highest power of band dispersion (n). Here, we consider three-dimensional crystals with spin-orbit coupling, respecting time-reversal symmetry. We consider single-point degeneracy in k space, so the materials with line nodes are not included. Some cases, e.g., g and n , are forbidden because of the restriction of crystal symmetries. Some cases are predicted to exist, but there is no material realization yet (marked by "?" in the table). The materials with asterisks have hypothetical configurations, while the rest of the examples (including our work) have been synthesized as single crystals.

that all the quasi-1D compounds have strong dispersions along the c axis and flat in-plane dispersions. Comparatively, the compounds with heavier A and X elements tend to have stronger in-plane dispersions because of the relativistic effects.

APPENDIX C: SPACE GROUPS [illegible] HOS [illegible] CUBIC DIRAC FERMIONS

Here, we use symmetry analysis to show how nonsymmorphic symmetry ensures fourfold degeneracy, i.e., the Dirac point, at certain time-reversal invariant (TRI) k points in a spin-orbit system preserving both inversion symmetry P and time-reversal symmetry T. Then, we show that out of 230 space groups, only P =m (No. 176) and P =mcc (No. 192) have appropriate symmetries to host cubic Dirac fermions.

In a spin-orbit system, the anti-unitary operator T behaves as $T^2 = -$, leading to Kramers degeneracy. Together with inversion symmetry, it turns out that all the energy bands are twofold degenerate with the two components related to each other by PT, i.e., $\psi(\boldsymbol{k},\sigma)$ and $PT\psi(\boldsymbol{k},\sigma) = \psi(\boldsymbol{k},-\sigma)$, which is known as spin degeneracy. Therefore, to achieve fourfold degeneracy, we need an extra pair of states $L\psi$ and $PTL\psi$ with $[L,H] = 0$ that differ with ψ and $PT\psi$, while L is a Hermitian symmetry operator of the system. We are thus looking for another Hermitian symmetry operator $\mathcal{A}$ to fulfill the condition $\{A, A_{PT}\} \cap \{A_L, A_{LPT}\} = \emptyset$, where A is the eigenvalue of ψ under $\mathcal{A}$. Thus, we get two pairs of bands $\{\psi, PT\psi\}$ and $\{L\psi, PTL\psi\}$ that have different eigenvalues of $\mathcal{A}$, so they must have a band crossing rather than a gap opening. The task is basically to find the two operators L and $\mathcal{A}$, and the degeneracy will happen at the k points that are invariant under these two symmetry operations. For example, if the k points that are invariant under both L and $\mathcal{A}$ form a line, the system is thus a nodal-line semimetal.

Without adding new symmetries, we first let L = P. Since the P operator reverses the momentum, there are only eight TRI k points in the BZ that are P invariant. Now, we are looking for the operator $\mathcal{A}$ that fulfills

$$\{A, A_{PT}\} \cap \{A_P, A_T\} = \emptyset. \tag{C1}$$

We next consider the most common twofold symmetries for $\mathcal{A}$ that all the TRI k points can preserve, which have two eigenvalues. From Eq. (C1), we have $A = -A_P$, indicating

$$\mathcal{A}P\psi = A_P P\psi = -PA\psi = -P\mathcal{A}\psi, \tag{C2}$$

which leads to the anticommutation relationship

$$\{\mathcal{A}, P\} = 0. \tag{C3}$$

Given that P commutes with any point-group operations, we conclude that $\mathcal{A}$ contains a nonsymmorphic symmetry that is a combination of point-group operation and fractional translation. In addition, from Eq. (1), there is another condition $A = -A_T$. Considering $[\mathcal{A}, T] = 0$, we have

$$\mathcal{A}T\psi = T\mathcal{A}\psi = TA\psi = -TA_T\psi = A_T T\psi, \tag{C4}$$

which indicates $A_T = i$ and thus

$$\mathcal{A}^2 = -. \tag{C5}$$

Therefore, the symmetry operation $\mathcal{A}$ that fulfills Eqs. (C3) and (C5) ensures a DP in certain TRI k points.

Combining three symmetry filters for cubic Dirac semimetal (i.e., inversion, C , and nonsymmorphic symmetry), only four possibilities [P =m (No. 176), P =mcc (No. 192), P =mcm (No. 193), and P =mmc (No. 194)] are left. All of these space groups have DPs at the four TRI k points (one A point and three L points) within the $k_z = \pi$ plane. For space groups No. 176, No. 193, and No. 194, there is an axis symmetry $\{C_2 | 0,0,1/2\}$, which transforms (x, y, z) in position space to (−x, −y, z +1/2). Considering the combination symmetry $\mathcal{A} = P\{C_2 | 0,0,1/2\}$, it is easy to test that $[\mathcal{A}, P] = 0$ in the $k_z = 0$ plane and $\{\mathcal{A}, P\} = 0$ in the $k_z = \pi$ plane. On the other hand, $\mathcal{A}^2$ preserves (x, y, z) while it rotates spin by 2π, leading to a minus sign, $\mathcal{A}^2 = -$. Therefore, $\mathcal{A}$ protects the fourfold degeneracy at the four TRI k points within the $k_z = \pi$ plane. However, space groups No. 193 and No. 194 have three mirror planes parallel to the C axis, posing extra symmetry conditions that force three high-symmetry lines to be degenerate. Here, we still take $\mathcal{A} = P\{C_2 | 0,0,1/2\}$ but $L = M_x$, which transforms (x, y, z) in position space to (−x, y, z). The commutation relationship then reads $\{\mathcal{A}, M_x\} = 0$ and $[\mathcal{A}, PTM_x] = 0$ in the $k_z = \pi$ plane. In this case, $\mathcal{A}$ and L keep the whole $k_x = 0$ line, as well as another two lines related by C symmetry in the $k_z = \pi$ plane, rendering the system a nodal-line or nodal-ring semimetal.

On the other hand, space group P =mcc (No. 192) has six glide reflection planes that all contain the C axis, and here we take $\{M_x | 0,0,1/2\}$, which transforms (x, y, z) to (−x, y, z +1/2). Similarly, considering the combination symmetry $\mathcal{A} = P\{M_x | 0,0,1/2\}$, we also have $\{\mathcal{A}, P\} = 0$ in the $k_z = \pi$ plane and $\mathcal{A}^2 = -$, which protects only four DPs and no extra symmetries for more degenerate k points. Finally, we reach the conclusion that out of 230 space groups, only P =m (No. 176) and P =mcc (No. 192)

preSoups6.113D45763Goups74967D48(mcc1Tfmor7reW47.776Jori42

[3] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, *T ca Sm eta a d Fer A c S ace State t e E ect c St ct e Py c e I date* , Phys. Rev. B **83**, 205101 (2011).

[4] Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, and Z. Fang, *D ac Sm eta a d T - ca P a e T a t A B (A Na, K, Rb)*, Phys. Rev. B **85**, 195320 (2012).

[5] B. Bradlyn, J. Cano, Z. Wang, M. G. Vergniory, C. Felser, R. J. Cava, and B. A. Bernevig, *Bey d D ac a d Wey Fer : U c e t a Q a a t e C e t a C y ta* , Science **353**, 5037 (2016).

[6] G. Xu, H. Weng, Z. Wang, X. Dai, and Z. Fang, *C e Sm eta a d t e Q a t ed A a Ha E ect* $HgCr_2$ *Bey 8(B)T .M t TD.8(e ,)-40.(X.8-.4(Sm eta)-4 d)-499.T TJ 9(E .4(B0.b)-8(4Fby9-.4(P 3(Q c)9(G 80T90 99.0(.0TD(,)Tj.8849.884. c .98*