Real spin and pseudospin topologies in the noncentrosymmetric topological nodal-line semimetal CaAgAs

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We present the topology of spin-split Fermi surface of CaAgAs as determined by de Haas-van Alphen (dHvA) effect measurements combined with ab initio calculations. We have determined the torus-shaped nodal-line Fermi surface from the dHvA oscillations of β and γ orbits. The former orbit encircles the nodal-line, while the latter does not. Nevertheless, a nontrivial Berry phase is found for both orbits. The nontrivial phase of β arises from the orbital characters, which can be expressed as a pseudospin rotating around the nodal-line. On the other hand, the phase of γ is attributed to the vortex of real spin texture induced by an antisymmetric spin-orbit interaction. Our result demonstrates that both the real- and pseudo-spin textures are indispensable in interpreting the electronic topology in noncentrosymmetric nodal-line semimetals.

Nodal-line semimetals (NLSMs) are a class of topological materials characterized by a linearly dispersing band-crossing along a continuous line in the three-dimensional $k$-space [1, 2]. Various intriguing quantum phenomena are predicted in NLSM [3–15]. Although numerous materials are proposed as the NLSM [16–33], most candidates accompany trivial bands around the Fermi level ($E_F$), which screen the characteristic properties arising from the nodal-line (NL) bands. CaAgAs is one of the ideal NLSM which has only a circular NL band around the $E_F$ [34–36].

CaAgAs crystallizes in the ZrNiAs-type structure with the noncentrosymmetric space group $P6_2m$ (#189) [37]. As depicted in Fig. 1(a), it consists of four crystallographic sites: Ca, Ag, As1, and As2. An ab initio calculation shows that the conduction and valence bands mainly consist of Ag 5s and As2 4pz characters, respectively, which overlap with each other around the Γ point [see Fig. 1(b)]. These orbitals have opposite eigenvalues for the (0001) mirror operation [34] and can be regarded as opposite pseudospins. Consequently, the bands cannot hybridize at $k_z = 0$ (and π) without spin-orbit interaction (SOI), leading to the quarternary degenerated NL as depicted in Fig. 1(c). The perturbation of the SOI allows the hybridization and opens a gap of $\Delta \sim 75$ meV, giving rise to the strong topological insulator state for a Fermi energy ($E_F$) locating in the middle of the gap [34, 38]; though, the NL topology still resides when $E_F$ is away from the gap [35, 39]. Experimentally, the linear dispersions associated with the NL bands are confirmed by angle-resolved photoemission spectroscopy [40–42]. However, the effect of spin splitting has not been addressed. The lack of inversion symmetry lifts the spin degeneracy via an antisymmetric SOI (ASOI), inducing an additional nontrivial feature of the real spin degree of freedom as in the Rashba and Dresselhaus systems [43, 44]. Although the ASOI in CaAgAs is small [34], it is still accessible in terms of the quantum oscillation. Thus, we studied the comprehensive picture of the spin-split Fermi surface (FS) of the NL in CaAgAs. The nontrivial Berry phase arising from the real spin and pseudospin are found depending on the trajectory on the torus-shaped FS.

Single crystals of CaAgAs were grown as described in Ref. [42]. The crystals were confirmed to be a single domain by the X-ray diffraction technique. The de Haas-van Alphen (dHvA) effect on the magnetic torque $\tau$ was measured with the piezoresistive cantilever [45], which was rotated in the magnetic field $B$ within the $ac$-plane, as shown in Fig. 1(c); see Supplemental Material (SM) for details [46]. The field angle $\theta$ is measured from the $a$-axis. The band-structure, FS, spin polarization and dHvA frequencies ($F$’s) are calculated from the fully relativistic electronic structure based on the density functional theory (DFT) [60] and the tight-binding method [61]; see SM [46]. For comparison, we used both the Perdew, Burke, and Ernzerhof (PBE) potential [62] and the Heyd, Scuseria, and Ernzerhof (HSE06) hybrid potential [63, 64] in the DFT calculation.

Theoretically, an oscillatory contribution to the mag-

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**FIG. 1.** (Color online) (a) Crystal structure of CaAgAs viewed along $c$-axis. $z$-parameter of each sites is given at the bottom. (b) Band structure near the Fermi level. Ag 5s and As2 4pz characters are indicated by colors. The dashed line indicates the experimental Fermi level $E_F = -230$ meV measured from the ideal Fermi level $E_{F0}$. (c) The red circle around the Γ indicates the NL in the Brillouin zone. The definitions of $\tau$ and $\theta$ are given.
The spin-polarization magnetic torque from an extremal orbit $O$ about the spin-
nondegenerate FS can be described as

$$\Delta \tau = CB^{3/2} \frac{\partial F_\theta}{\partial \theta} R_T R_D \sin \left[ 2\pi \left( \frac{F_\theta}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} + \phi_Z + \phi_B \right],$$

(1)

where $C$ is a positive coefficient, $\phi_B$ is a Berry phase, and the $\pm$ sign is positive (negative) when $O$ is a minimum (maximum) [65]. Higher harmonics are neglected. The frequency $F_\theta$ relates with the cross-sectional area $S_0$ at $B = 0$ of the orbit as $F_\theta = hS_0/2\pi e$. The temperature and Dingle reduction factors are given by $R_T = \xi / \sinh \xi$ and $R_D = \exp( - \xi_D )$, respectively, where $\xi_D = 2\pi^2 k_B T_D m^* / e^2 B$, $T_D$ is a Dingle temperature, and $m^*$ is a cyclotron effective mass. The Zeeman energy of electron spin causes a basically linear-in-$B$ change in the orbit area, which does not change the apparent frequency of the oscillation but gives rise to a constant phase shift $\phi_Z$ expressed as

$$\phi_Z = \int_O \frac{g\hbar \sigma_B}{4m_e v_\perp} |d\mathbf{k}|,$$

(2)

with $O$ carrying a clockwise orientation [66]. Here $g$ is a $g$-factor, $m_e$ is the free electron mass, and $v_\perp$ is a Fermi velocity along $B \times d\mathbf{k}$. $\sigma_B$ is given by $\sigma_B = \mathbf{B} \cdot \mathbf{P}$ with the spin-polarization $\mathbf{P} = \langle \sigma \rangle$.

Figure 2(a) shows $\tau(B)$ at $\theta = 27.1^\circ$, which is proportional to $B^2$ as expected for paramagnets. The oscillatory components $\Delta \tau$ are obtained by subtracting a second-order polynomial background $\tau_{\text{PC}}$ from $\tau$, where dHvA oscillations are discernible above $\sim 10$ T. Figure 2(b) shows Fourier transforms of oscillations for various field directions $\theta$. The ASOI-induced spin splitting is too small to be resolved. We also plot $F'$'s determined by fitting the oscillations at high fields with Eq. (S1) as circles. Here, we neglect the spin splitting of the $F'$'s and hence the determined $F'$'s are the averages of the split frequencies. The $F'$'s increase as $\theta$ approaches to 90°.

Figure 3(a) represents the spin-split FS calculated with HSE06 potential and $E_F = -230$ meV (explained below). The FS of the circular NL becomes torus due to the self-doped hole carriers [40]. There are four types of extremal orbits: $\alpha$, $\beta$, $\gamma$, and $\delta$; the $\alpha$ and $\beta$ ($\gamma$ and $\delta$) orbits correspond to the minimum (maximum) cross-sections. The ASOI splits the torus into two tori, one nesting inside the other [Figure 3(b) shows cross-sections schematically]. Accordingly, the four orbits also split, but the splitting is small, of the order of 1% of the cross-sectional areas. The Kramers degeneracy is preserved along $\Gamma$-K lines in consequence of the $D_{5d}$ point-group symmetry.

Since the oscillation amplitude around $B \parallel a$ is small due to the small $\partial F_\theta / \partial \theta$ factor in Eq. (S1), we measured $m^*$ at $\theta = 36.4^\circ$. Figure 2(c) shows the temperature dependence of the oscillation amplitudes of $F_\beta(36.4^\circ) = 118$ T and $F_\gamma(36.4^\circ) = 283$ T. $m_\gamma(36.4^\circ)/m_e = 0.095(9)$, $m_\gamma(36.4^\circ)/m_e = 0.130(8)$ are obtained by fitting the data with $R_T$. Approximating the angular dependence of the $\beta$ orbit as the one of a cylinder along $a$-axis, we have $F_\beta(0^\circ) \approx F_\beta(\theta) \cos \theta = 95.0$ T and $m_\gamma(0^\circ) \approx m_\gamma(\theta) \cos \theta = 0.076(8)$, which correspond to $k_F = 5.4 \times 10^{-2}$ $\AA^{-1}$ and $\tau_F = 8.1(8) \times 10^5$ m/s of the $\beta$ cross-section. Assuming a linear- (parabolic-) dispersion perpendicular to the NL, the $E_F$ is estimated as $-288(29) [-144(14)]$ meV; the linear-dispersion gives closer value to $-230$ meV from the $ab$ initio calculation, as expected. The radius of the circular NL $R_T$ is estimated to be $8.4 \times 10^{-2}$ $\AA^{-1}$ from the geometrical relation of the orbits of $F_\beta(36.4^\circ)$ and $F_\gamma(36.4^\circ)$ and assuming an ideally torus-shaped FS. Accordingly, the car-
carrier concentration is estimated from the volume of the torus as $4\pi^2 k_B^2 (2\pi)^3 = 3.9 \times 10^{19}$ cm$^{-3}$, which is smaller than previous reports obtained by the Hall effect [35, 41, 42, 68].

Having identified the FS, we visualize, in Fig. 3(c, d), the calculated polarization of the real spin $P$ and the pseudospin $P_p$ on the FS obtained with the HSE06 and $E_F = -230$ meV determined above. Here, the up (down) of the pseudospin is defined as the orbital character of the Ag 5$s$ (As2 4$p_z$). The $P_p$ is evaluated with the effective eigenspinor constructed by projecting the calculated tight-binding wavefunction on the two orbital bases, $|\text{Ag 5}s\rangle$ and $|\text{As2 4}p_z\rangle$. The real spin has a vortex texture around the $\Gamma$–K line, while the pseudospin has one around the NL.

To reveal the nontrivial nature of the electronic states, we analyzed the phases of the $\beta$ and $\gamma$ oscillations. In the limit of $B \to 0$, neither of the $\beta$ and $\gamma$ orbits is self-constrained by time-reversal operation; there is a time-reversal symmetric (TRS) pair of orbits on each of the spin-split FSs as indicated in Fig. 3(a). Therefore, each of the $\beta$ and $\gamma$ oscillations consists of the interference of four individual oscillations.

The $\phi_{B}$ of an individual oscillation can be considered as a sum of the real spin contribution $\phi_{B,r}$ and the pseudospin contribution $\phi_{B,p}$. Then, the dHvA oscillations from the spin-split pair of orbits have split frequencies $F_0 \pm \Delta F_0$ and the same (opposite) sign of $\phi_{B,p}$ ($\phi_Z$ and $\phi_{B,r}$). Similarly, those from the TRS pair of orbits have the same $F$'s and the opposite sign of $\phi_Z$, $\phi_{B,r}$ and $\phi_{B,p}$.

In addition, because $\Delta \ll |E_F|$, the $\phi_{B,p}$ is constrained to $N\pi$ with $N$ being the winding number of the pseudospin [39, 69, 70]. Then, the sum of Eq. (S1) for the four individual oscillations becomes

$$\Delta\tau_D = 4CB^{3/2} \frac{\partial F_0}{\partial B} R_T R_D \cos \left(2\pi \frac{\Delta F_0}{B}\right) \cos (\phi_Z + \phi_{B,r}) \cos (\phi_{B,p}) \sin \left[2\pi \left(\frac{F_0}{B} - \frac{1}{2}\right) \pm \frac{\pi}{4}\right],$$

where $O = \beta$, $\gamma$ and $F_0 (2\Delta F_0)$ is the mean (difference) of $F$’s for the spin-split pair of orbits [46]. The first cosine factor describes the beating between the spin-split $F$’s, while the other cosine factors change sign depending on $\phi_Z$, $\phi_{B,r}$, and $\phi_{B,p}$. In the following, we determine $\phi_{B,r}$ and $\phi_{B,p}$ for each of $\beta$ and $\gamma$ based on Eq. (3).

To consider the $\beta$ and $\gamma$ oscillations ($\Delta\tau_\beta$, $\Delta\tau_\gamma$) separately, we extract each of them from the observed oscillation $\Delta\tau$ as follows: We first plot the $\Delta\tau$ as a function of $B^{-1}$ in Fig. 4(a). Then, the $\beta$ and $\gamma$ oscillations are effectively suppressed by applying two boxcar smoothings with the box width of $F_0^{-1}$ and $F_0^{-1}$. The residual $\Delta\tau_{\text{res}}$ contains a background from the cantilever. The $\Delta\tau_\beta$ is obtained from $\Delta\tau - \Delta\tau_{\text{res}}$ by similarly applying one boxcar smoothing with the box width of $F_0^{-1}$ to remove the $\gamma$ oscillation. Finally, $\Delta\tau = \Delta\tau_{\text{res}} - \Delta\tau_\beta$ provides $\Delta\tau_\gamma$. The results are also shown in Fig. 4(a). The Fourier transformations in Fig. 4(b) confirms the validity of the extraction. Figures 4(c, d) shows $\Delta\tau_\gamma$ and $\Delta\tau_{\text{res}}$ as a function of $F/B \pm 1/8 - 1/4$. The sine factor in Eq. (3) becomes minima at integers of this abscissa.

Let us start with the $\gamma$ oscillation. At $\theta = 32.1^\circ$, the sign of the oscillation changes at the specific field $B_{\text{node}}$, indicated by arrows in Fig. 4(c); the oscillation has tops (bottoms) at integers of the abscissa on the left (right) of $B_{\text{node}} (B > B_{\text{node}})$ $(|B < B_{\text{node}}|)$. An in-phase intensity with $\cos (2\pi x)$ in $\Delta\tau_\gamma$,

$$I(x') = \int_{x'-1/2}^{x'+1/2} \Delta\tau_\gamma(x) \cos (2\pi x) dx,$$
ranging from 8 T to 17.8 T at each $\theta$. If $n_{\gamma} > 2$, the neighboring node $n'_{\gamma} = n_{\gamma} \pm 1$ should be observed at $B_{\text{node}}' = 2 - (2n'_{\gamma} + 1)/(2n_{\gamma} + 1)B_{\text{node}}$; however, no such node exists [see red dashed curves in Fig. 4(c), which show expected neighboring node positions when $n_{\gamma}$ were 2 or 3].

The geometrical relation between the $\gamma$ and $\beta$ orbits further reduces the possibility of the $n_{\gamma}$. If $n_{\gamma} = 1 (2)$, $\Delta F_\gamma = 2.72 - 3.40 (8.16 - 10.20)$ T for $\theta = 32.1 - 47.1^\circ$. Assuming a $k$-independent energy of ASOI $E_{\text{ASOI}}$, this corresponds to $E_{\text{ASOI}} = 1.37 (4.12)$ meV. Then, the splitting of the $\beta$ oscillation ranges $\Delta F_{\beta} = 1.26 - 1.64 (3.78 - 4.93)$ T and the associated position of the beating node for $n_{\beta} = 1$ is estimated as $F_{\beta}/B_{\text{node}} = 20.8 - 20.3 (6.93 - 6.77)$. The dashed curve in Fig. 4(d) shows the expected node positions when $n_{\gamma}$ were 2. The $\beta$ oscillation neither shows node nor is damped near the dashed curve at $\theta = 17.1 - 32.1^\circ$ where the oscillations are strong enough, indicating $n_{\beta} = 1$ ($F_{\beta}/B \sim 20.6$ is out of our observation of the dHvA oscillations).

The so determined $n_{\gamma} = 1$ allows us to find the Berry phase of the $\gamma$ oscillation from Eq. (3). The sign of the $\cos (2\pi \Delta F_{\gamma}/B)$ factor is positive for $B > B_{\text{node}}$. Since the $\partial F_{\gamma}/\partial \theta$ factor is also positive, the residual factor, $\cos (\phi_{Z} + \phi_{B,r}) \cos (\phi_{B,p})$, is negative. Moreover, since the $\gamma$ orbit is self-constrained by the (0110) mirror operation as long as $B$ is rotated within the $k_y - k_z$ plane, the $\phi_{B,r}$ is constrained to the integer-multiple of $\pi$ [71] and the $\phi_{Z}$ is always 0 [46]. Therefore, the $\gamma$ orbit has a nontrivial Berry phase arising from either of $\phi_{B,r}$ or $\phi_{B,p}$. Since the $\gamma$ orbit topologically does not encircle the NL, $\phi_{B,p} = 0$ and $\phi_{B,r} = \pi$ are concluded. This result agrees with the expectation from the fact that the $\gamma$ orbit encircles three $\Gamma$–$K$ lines, leading to $\phi_{B,r} = 3\pi$ (mod $2\pi$). Thus, the nontrivial Berry phase of the $\gamma$ orbit is attributed to the real spin texture.

Similarly, the Berry phase of the $\beta$ oscillation is determined. As mentioned above, the observed $\beta$ oscillations are in $B > B_{\text{node}}$ for $n_{\beta} = 1$; hence, $\cos (2\pi \Delta F_{\beta}/B) > 0$. Considering $\partial F_{\beta}/\partial \theta > 0$, the sign of the $\cos (\phi_{Z} + \phi_{B,r}) \cos (\phi_{B,p})$ factor is identified as negative within $\theta = 17.1 - 47.1^\circ$, where we observe the discernible $\beta$ oscillation. In the case of the $\beta$ orbit, the constraint on the $\phi_{B,r}$ [71] and $\phi_{Z} = 0$ are assured only at $\theta = 0^\circ$ where the orbit is self-constrained by the (0001) mirror operation. However, it can be shown from the elaborate spin-zero analysis that the sign of $\cos (\phi_{Z} + \phi_{B,r})$ factor does not change in $|\theta| \leq 47.1^\circ$ [46]. Consequently, the $\beta$ orbit also has a nontrivial Berry phase at $\theta = 0^\circ$ owing to either of the $\phi_{B,r}$ or $\phi_{B,p}$. Contrary to the $\gamma$ orbit, the $\beta$ orbit encircles no $\Gamma$–$K$ line but encircles the NL. Therefore, $\phi_{B,p} = \pi$, which is attributed to the NL and evidences the NL topology of the orbital characters.

In conclusion, we have determined the torus-shaped FS in CaAgAs via quantum-oscillation measurements. We have found a nontrivial Berry phase for both $\beta$ and $\gamma$ orbits. The former encircles the NL and hence the observed Berry phase is ascribable to the pseudospin texture around the NL. The latter orbit topologically does
not encircle the NL. By combining \textit{ab initio} calculations, we have demonstrated that the Berry phase associated with \(\gamma\) originates from the real spin texture where the spin direction rotates around the \(\Gamma-K\) line in the Brillouin zone. Our results suggest that noncentrosymmetric NL semimetals provide fertile ground for investigating new quantum phenomena arising from synergy between spin and orbital pseudospin physics.

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[1] A. A. Burkov, M. D. Hook, and L. Balents, Topological nodal semimetals, \textit{Phys. Rev. B} \textbf{84}, 235126 (2011).
[2] C. Fang, H. Weng, X. Dai, and Z. Fang, Topological nodal line semimetals, \textit{Chinese Phys. B} \textbf{25}, 117106 (2016).
[3] N. B. Kopnin, T. T. Heikkilä, and G. E. Volovik, High-temperature surface superconductivity in topological flat-band systems, \textit{Phys. Rev. B} \textbf{83}, 220503(R) (2011).
[4] J.-W. Rhim and Y. B. Kim, Landau level quantization and almost flat modes in three-dimensional semimetals with nodal ring spectra, \textit{Phys. Rev. B} \textbf{92}, 045126(R) (2015).
[5] A. K. Mitchell and L. Fritz, Kondo effect in three-dimensional Dirac and Weyl systems, \textit{Phys. Rev. B} \textbf{92}, 121109(R) (2015).
[6] Y. Huh, E.-G. Moon, and Y. B. Kim, Long-range Coulomb interaction in nodal-ring semimetals, \textit{Phys. Rev. B} \textbf{93}, 035138 (2016).
[7] L.-K. Lim and R. Moessner, Pseudospin Vortex Ring with a Nodal Line in Three Dimensions, \textit{Phys. Rev. Lett.} \textbf{118}, 016401 (2017).
[8] J. P. Carbotte, Optical response of a line node semimetal, \textit{J. Phys.: Condens. Matter} \textbf{29}, 045301 (2017).
[9] S. T. Ramamurthy and T. L. Hughes, Quasipotential electromagnetic response of line-node semimetals, \textit{Phys. Rev. B} \textbf{95}, 075138 (2017).
[10] J. Liu and L. Balents, Correlation effects and quantum oscillations in topological nodal-loop semimetals, \textit{Phys. Rev. B} \textbf{95}, 075426 (2017).
[11] S. P. Mukherjee and J. P. Carbotte, Transport and optics at the node in a nodal loop semimetal, \textit{Phys. Rev. B} \textbf{95}, 214203 (2017).
[12] S. V. Syzranov and B. Skinner, Electron transport in nodal-line semimetals, \textit{Phys. Rev. B} \textbf{96}, 161105(R) (2017).
[13] S. Barati and S. H. Abedinpour, Optical conductivity of three and two dimensional topological nodal-line semimetals, \textit{Phys. Rev. B} \textbf{96}, 155150 (2017).
[14] W. B. Rui, Y. X. Zhao, and A. P. Schnyder, Topological transport in Dirac nodal-line semimetals, \textit{Phys. Rev. B} \textbf{97}, 161113(R) (2018).
[15] J. Li, H. Ma, Q. Xie, S. Feng, S. Allah, R. Li, J. Dong, D. Li, Y. Li, and X.-Q. Chen, Topological quantum catalyst: Dirac nodal line states and a potential electrocatalyst of hydrogen evolution in the TiSi family, \textit{Sci. China Mater.} \textbf{61}, 23 (2018).
[16] G. Xu, H. Weng, Z. Wang, X. Dai, and Z. Fang, Chern Semimetal and the Quantized Anomalous Hall Effect in HgCr\(_2\)Se\(_4\), \textit{Phys. Rev. Lett.} \textbf{107}, 186806 (2011).
[17] G. Bian, T.-R. Chang, H. Zheng, S. Velury, S.-Y. Xu, T. Neupert, C.-K. Chiu, S.-M. Huang, D. S. Sanchez, I. Belopolski, N. Alidoust, P.-J. Chen, G. Chang, A. Bansil, H.-T. Jeng, H. Lin, and M. Z. Hasan, Drumhead Surface States and Topological Nodal-Line Fermions in T-TaS\(_2\), \textit{Phys. Rev. B} \textbf{93}, 121113(R) (2016).
[18] G. Bian, T.-R. Chang, R. Sankar, S.-Y. Xu, H. Zheng, T. Neupert, C.-K. Chiu, S.-M. Huang, G. Chang, I. Belopolski, D. S. Sanchez, M. Neupane, N. Alidoust, C. Liu, B. Wang, C.-C. Lee, H.-T. Jeng, C. Zhang, Z. Yuan, S. Jia, A. Bansil, F. Chou, H. Lin, and M. Z. Hasan, Topological nodal-line fermions in spin-orbit metal PbTaS\(_2\), \textit{Nature Commun.} \textbf{7}, 10556 (2016).
[19] L. S. Xie, L. M. Schoop, E. M. Seibel, Q. D. Gibson, W. Xie, and R. J. Cava, A new form of Cs\(_3\)P\(_2\) with a ring of Dirac nodes, \textit{APL Materials} \textbf{3}, 083602 (2015).
[20] R. Yu, H. Weng, Z. Fang, X. Dai, and X. Hu, Topological Node-Line Semimetal and Dirac Semimetal State in Antiperovskite Cs\(_3\)Pd\(_2\)N, \textit{Phys. Rev. Lett.} \textbf{115}, 036807 (2015).
[21] Y. Kim, B. J. Wieder, C. L. Kane, and A. M. Rappe, Dirac Line Nodes in Inversion-Symmetric Crystals, \textit{Phys. Rev. Lett.} \textbf{115}, 066806 (2015).
[22] L. M. Schoop, M. N. Ali, C. Strafer, A. Topp, A. Varykhalov, D. Marchenko, V. Dupple, S. S. P. Parkin, B. E. Votsch, and C. R. Ast, Dirac cone protected by non-symmmorphic symmetry and three-dimensional Dirac line node in ZrSiS, \textit{Nature Commun.} \textbf{7}, 11696 (2016).
[23] M. Neupane, I. Belopolski, M. M. Hosen, D. S. Sanchez, R. Sankar, M. Szwakowska, S.-Y. Xu, K. Dimitri, N. Dhalak, P. Maldonado, P. M. Oppeneer, D. Kaczorowski, F. Chou, M. Z. Hasan, and T. Durakiewicz, Observation of topological nodal fermion semimetal phase in ZrSiS, \textit{Phys. Rev. B} \textbf{93}, 214104(R) (2016).
[24] J. Hu, Z. Tang, J. Liu, X. Liu, Y. Zhu, D. Graf, K. Myhro, S. Tran, C. N. Lau, J. Wei, and Z. Mao, Evidence of Topological Nodal-Line Fermions in ZrSiS\(_2\) and ZrS\(_2\)Te, \textit{Phys. Rev. Lett.} \textbf{117}, 016602 (2016).
[25] D. Takane, Z. Wang, S. Souma, K. Namayama, C. X. Trang, T. Sato, T. Takahashi, and Y. Ando, Dirac-node arc in the topological line-node semimetal HfSiS, \textit{Phys. Rev. B} \textbf{94}, 214108(R) (2016).
[26] C. Chen, X. Xu, J. Jiang, S.-C. Wu, Y. P. Qi, L. X. Yang, M. X. Wang, Y. Sun, N. B. M. Schröter, H. F. Yang, L. M. Schoop, Y. Y. Lv, J. Zhou, Y. B. Chen, S. H. Yao, M. H. Lu, Y. F. Chen, C. Felser, B. H. Yan, Z. K. Liu, and Y. L. Chen, Dirac line nodes and effect of spin-orbit coupling in the nonsymmmorphic critical semimetals MSi\(_3\)S\(_3\) (\(M = \text{Hf, Zr}\)), \textit{Phys. Rev. B} \textbf{95}, 125126 (2017).
[27] H. Weng, Y. Liang, Q. Xu, R. Yu, Z. Fang, X. Dai, and Y. Kawazoe, Topological node-line semimetal in three-dimensional graphene networks, \textit{Phys. Rev. B} \textbf{92}, 045108 (2015).
[28] K. Mullen, B. Uchoa, and D. T. Glatzhofer, Line of Dirac Nodes in Hyperhoneycomb Lattices, \textit{Phys. Rev. Lett.} \textbf{115}, 026403 (2015).
[29] X. Zhang, Z.-M. Yu, X.-L. Sheng, H. Y. Yang, and S. A. Yang, Coexistence of four-band nodal rings and triply degenerate nodal points in centrosymmetric metal diborides, \textit{Phys. Rev. B} \textbf{95}, 235116 (2017).
[30] X. Zhang, B. Fu, L. Jin, X. Dai, G. Liu, and Y. Yao,
Topological Nodal Line Electrides: Realization of an Ideal Nodal Line State Nearly Immune from SpinOrbit Coupling, J. Phys. Chem. C 123, 25871 (2019).

[31] Q.-F. Liang, J. Zhou, R. Yu, Z. Wang, and H. Weng, Node-surface and node-line fermions from nonsymmorphic lattice symmetries, Phys. Rev. B 93, 085427 (2016).

[32] Y. Wu, L.-L. Wang, E. Mun, D. D. Johnson, D. Mou, L. Huang, Y. Lee, S. L. Bud’ko, P. C. Canfield, and A. Kaminski, Dirac node arcs in PtSn₄, Nature Phys. 12, 667 (2016).

[33] S. A. Ekahana, S.-C. Wu, J. Jiang, K. Okawa, D. Prabhakaran, C.-C. Hwang, S.-K. Mo, T. Sasagawa, C. Felser, B. Yan, Z. Liu, and Y. Chen, Observation of nodal line in non-symmorphic topological semimetal InBi, New J. Phys. 19, 065007 (2017).

[34] A. Yamakage, Y. Yamakawa, Y. Tanaka, and Y. Okamoto, Line-Node Dirac Semimetal and Topological Insulating Phase in Noncentrosymmetric Pnictides CaAgX (X = P, As), J. Phys. Soc. Jpn. 85, 013708 (2016).

[35] E. Emmanouilidou, B. Shen, X. Deng, T.-R. Chang, A. Shi, G. Kotliar, S.-Y. Xu, and N. Ni, Magnetotransport properties of the single-crystalline nodal-line semimetal candidates CaFX (T = Ag, Cd; X = As, Ge), Phys. Rev. B 95, 245113 (2017).

[36] N. Xu, Y. T. Qian, Q. S. Wu, G. Auttés, C. E. Matt, B. Q. Lv, M. Y. Yao, V. N. Strocov, E. Pomjakushina, K. Conder, N. C. Plumb, M. Radovic, O. V. Yazyev, T. Qian, H. Ding, J. Mesot, and M. Shi, Trivial topological phase of CaAgP and the topological nodal-line transition in CaAg(PₓAs₁₋ₓ), Phys. Rev. B 97, 161111 (R) (2018).

[37] A. Mewis, CaAgP und CaAgAs -Zwei Verbindungen mit Fe₂P-Struktur (CaAgP and CaAgAs -Two Compounds with Fe₂P-Structure), Z. Nat. B 34, 14 (1979).

[38] C. L. Kane and E. J. Mele, Quantum Spinn Hall Effect in Graphene, Phys. Rev. Lett. 95, 226801 (2005).

[39] C. Li, C. M. Wang, B. Wan, X. Wan, H.-Z. Lu, and X. C. Xie, Rules for Phase Shifts of Quantum Oscillations in Topological Nodal-Line Semimetals, Phys. Rev. Lett. 120, 146602 (2018).

[40] X.-B. Wang, X.-M. Ma, E. Emmanouilidou, B. Shen, C.-H. Hsu, C.-S. Zhou, Y. Zuo, R.-R. Song, S.-Y. Xu, G. Wang, L. Huang, N. Ni, and C. Liu, Topological surface electronic states in candidate nodal-line semimetal CaAgAs, Phys. Rev. B 96, 161112 (R) (2017).

[41] J. Nayak, N. Kumar, S.-C. Wu, C. Shekhar, J. Fink, E. D. L. Rienks, G. H. Fecher, Y. Sun, and C. Felser, Electronic properties of topological insulator candidate CaAgAs, J. Phys.: Condens. Matter 30, 045501 (2017).

[42] D. Takane, K. Nakayama, S. Souma, T. Wada, Y. Okamoto, K. Takenaka, Y. Yamakawa, A. Yamakage, T. Mitsuhashi, K. Horiba, H. Kumigashira, T. Takahashi, and T. Sato, Observation of Dirac-like energy band and ring-torus Fermi surface associated with the nodal line in topological insulator CaAgAs, npj Quantum Mater. 3, 1 (2018).

[43] S.-Q. Shen, Spin Hall effect and Berry phase in two-dimensional electron gas, Phys. Rev. B 70, 081311 (R) (2004).

[44] H. Murakawa, M. S. Bahramy, M. Tokunaga, Y. Kohama, C. Bell, Y. Kaneko, N. Nagaosa, H. Y. Hwang, and Y. Tokura, Detection of Berrys Phase in a Bulk Rashba Semiconductor, Science 342, 1490 (2013).

[45] E. Ohmichi and T. Osada, Torque magnetometry in pulsed magnetic fields with use of a commercial micro-cantilever, Rev. Sci. Instrum. 73, 3022 (2002).

[46] Supplemental Material [URL/DOI-TBA] is available for additional information on the details about the sign of \( \gamma \), the calculation method, the derivation of Eq. (3), the determination of \( B_{node} \), the effect of magnetic breakdown, the symmetrical constraints on \( \phi_\beta \), the variation of the real spin Berry phase in the \( \beta \) orbit, and the spin-zero analysis on the \( \beta \) oscillation. Refs. [47–59] are included.

[47] P. Gianozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carminati, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. D. Jr., A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Kucukbenli, M. Lazzери, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncè, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, J. Phys.: Condens. Matter 29, 465901 (2017).

[48] A. D. Corso, Pseudopotentials periodic table: From H to Pu, Comput. Mater. Sci. 95, 307 (2014).

[49] D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, Phys. Rev. B 88, 085117 (2013).

[50] M. Schlipf and F. Gygi, Optimization algorithm for the generation of ONCV pseudopotentials, Comp. Phys. Commun. 196, 36 (2015).

[51] P. Scherpelz, M. Govoni, I. Hamada, and G. Galli, Implementation and Validation of Fully Relativistic GW Calculations: Spin–Orbit Coupling in Molecules, Nanocrystals, and Solids, J. Chem. Theory. Comput. 12, 3523 (2016).

[52] P. M. C. Rourke and S. R. Julian, Numerical extraction of de Haas–van Alphen frequencies from calculated band energies, Comput. Phys. Commun. 183, 324 (2012).

[53] N. Kimura, H. Sano, M. Shirakawa, A. Ochiai, H. Funashima, and H. Harima, Orbital Crossing on Split Fermi Surfaces in Noncentrosymmetric Yb₃Sb₅, J. Phys. Soc. Jpn. 87, 114708 (2018).

[54] P. A. Frigeri, Superconductivity in crystals without an inversion center, Ph.D. thesis, ETH-Zürich (2005), original paper misprints a sign in the corresponding formula.

[55] D. Vanderbilt, Berry Phases in Electronic Structure Theory: Electric Polarization, Orbital Magnetization and Topological Insulators (Cambridge University Press, 2018) pp. 75–140.

[56] M. V. Kartsovnik, High magnetic fields: a tool for studying electronic properties of layered organic metals, Chem. Rev. 104, 5737 (2004).

[57] S. E. Sebastian, N. Harrison, and G. G. Lonzarich, Towards resolution of the Fermi surface in underdoped high-\( T_c \) superconductors, Rep. Prog. Phys. 75, 102501 (2012).

[58] T. Terashima, H. T. Hirose, D. Graf, Y. Ma, G. Mu, T. Hu, K. Suzuki, S. Uji, and H. Ikeda, Fermi Surface with Dirac Fermions in CaFeAsF Determined via Quantum Oscillation Measurements, Phys. Rev. X 8, 011014 (2018).

[59] Y. Obata, Y. Kohama, S. Matsuishi, and H. Hosono, Shubnikovde Haas oscillations in the three-dimensional Dirac fermion system Ca₂PbO, Phys. Rev. B 99, 115133
[60] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B864 (1964).

[61] A. A. Mostofia, J. R. Yatesb, G. Pizzif, Y.-S. Leec, I. Souzad, D. Vanderbilte, and N. Marzari, An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions, Comput. Phys. Commun. 185, 2309 (2014).

[62] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).

[63] G. Kresse and J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54, 11169 (1996).

[64] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).

[65] D. Shoenberg, Magnetic Oscillations in Metals, Cambridge Monographs on Physics (Cambridge University Press, 1984).

[66] A. Alexandradinata, C. Wang, W. Duan, and L. Glazman, Revealing the Topology of Fermi-Surface Wave Functions from Magnetic Quantum Oscillations, Phys. Rev. X 8, 011027 (2018).

[67] Y. H. Kwan, P. Reiss, Y. Han, M. Bristow, D. Prabhakaran, D. Graf, A. McCollam, S. A. Parameswaran, and A. I. Coldea, Quantum oscillations probe the Fermi surface topology of the nodal-line semimetal CaAgAs (2020), arXiv:2001.02434 [cond-mat.str-el].

[68] Y. Okamoto, T. Inohara, A. Yamakage, Y. Yamakawa, and K. Takenaka, Low Carrier Density Metal Realized in Candidate Line-Node Dirac Semimetals CaAgP and CaAgAs, J. Phys. Soc. Jpn. 85, 123701 (2016).

[69] G. P. Mikitik and Y. V. Sharlai, Manifestation of Berry’s Phase in Metal Physics, Phys. Rev. Lett. 82, 2147 (1999).

[70] L. Oroszlány, B. Dóra, J. Cserti, and A. Cortijo, Topological and trivial magnetic oscillations in nodal loop semimetals, Phys. Rev. B 97, 205107 (2018).

[71] This constraint is mentioned in Ref. [66] as the class II-A ($u = 1, s = 0$).
Supplemental Material: Real spin and pseudospin topologies in the noncentrosymmetric topological nodal-line semimetal CaAgAs

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I. SIGN OF MAGNETIC TORQUE

We measured the magnetic torque $\tau$ by using a piezoresistive cantilever (MouldLessCantilever SSI-SSML-PRC400, Seiko Instruments Inc.) [1]. The experimental setup is schematically illustrated in Fig. S1(a) together with the notations for the field angle $\theta$ and $\tau$. The sign of $\tau$ exerted on a sample is known from whether the resistance of the piezoresistor increases or decreases. The sign of $\tau$ is essential when discussing the phase of de-Haas van-Alphen (dHvA) oscillation; assigning a wrong sign of the oscillation shifts the phase by $\pi$ [2].

As mentioned in the main manuscript, the oscillation of $\bigcirc$ branch $\Delta \tau_0$ consists of four individual oscillations $\Delta \tau_{t,s}$. Here, $t = \pm 1$ denotes the time-reversal symmetric pair of orbits, and $s = \pm 1$ denotes the spin-split pair of orbits owing to the antisymmetric spin-orbit interaction (ASOI). By taking into account the relations of the oscillation phase and frequency among $\Delta \tau_{t,s}$ [13], the $\Delta \tau_{t,s}$ can be expressed in terms of the $t$ and $s$ as

$$\Delta \tau_{t,s} = CB^{3/2} \frac{\partial F_0}{\partial \theta} R_T R_D$$

$$\sin \left[ 2\pi \left( \frac{F_0 + s\Delta F_0}{B} - \frac{1}{2} \right) \right] \pm \frac{\pi}{4} + ts\phi_Z + ts\phi_{B,r} + t\phi_{B,p},$$

where $F_0$ ($2\Delta F_0$) is the mean (difference of) frequencies of the spin-split pair of orbits, and $\phi_{B,r}$ ($\phi_{B,p}$) is the real spin (pseudospin) contribution to the Berry phase. The sum of the four individual oscillations becomes

II. CALCULATION METHOD

The fully relativistic electronic structure was calculated based on density functional theory [2] as implemented in the Quantum ESPRESSO package [3]. For comparison, we used both the Perdew, Burke, and Ernzerhof (PBE) function [4] and the Heyd, Scuseria, and Ernzerhof (HSE06) hybrid function [5, 6] for exchange potential. A $6 \times 6 \times 9$ $k$-point mesh was used for the self-consistent field procedure. A plane-wave cutoff energy of 140 Ry and a fully relativistic projector augmented-wave method [7] were used for the calculation with the PBE potential, while a plane-wave cutoff energy of 55 Ry, fully relativistic norm-conserving pseudopotentials [8–10], and a $2 \times 2 \times 3$ $q$-point mesh were used for the calculation with the HSE06 potential. The difference of the cutoff energies is due to the different types of the pseudopotentials. The band-structure, Fermi surface, and spin polarizations are calculated by using the 54-orbital tight-binding model based on maximally localized Wannier functions constructed with the Wannier90 program [11]. The dHvA frequencies are calculated from the Fermi surface by using the algorithm described in Ref. [12].

III. INTERERENCE OF THE FOUR INDIVIDUAL OSCILLATIONS

FIG. S1. (a) Schematic of the experimental setup for the torque magnetometry utilizing a cantilever and the notations for $\theta$ and $\tau$. (b) Angular dependence of the $\tau$ measured at 17.8 T and 30 mK. The insets are the enlarged views of the angular variation of the dHvA oscillations.
FIG. S2. (a) $\gamma$ oscillation component $\Delta \gamma$ as a function of $B^{-1}$. The gray dotted lines are experimental data, whereas the bold red and blue curves are the fits with Eq. (S2) and Eq. (S4), respectively. Arrows indicate the positions of $B = B_{\text{node}}$. (b) Real spin polarization $P$ on the $\gamma$ orbit at $\theta = 50^\circ$. The $\gamma$ orbit is on $k_z$ plane at $k_z = 0.022$ (2$\pi$/Å), where $k_z = -\sin(50^\circ)k_x + \cos(50^\circ)k_y$ and $k_z = \cos(50^\circ)k_x + \sin(50^\circ)k_y$. The inset illustrates the relation between the $k_z$ and $k_x$ coordinates. The direction and color of the arrows indicate the in-plane and out-of-plane components of $|P|/P$, respectively. Green circles mark the candidates of the breakdown $k$ points where $P$ rotates quickly along the orbit.

\[
\Delta \tau_0 = \sum_{t,s=\pm 1} \Delta \tau_{t,s} \\
= 4CB^3/2\frac{\partial F_0}{\partial \theta} R_T R_D \left\{ \cos \left( 2\pi \frac{F_0}{B} \right) \cos (\phi_Z + \phi_{B,r}) \cos (\phi_{B,p}) \sin \left[ 2\pi \left( \frac{F_0}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right] \\
- \sin \left( 2\pi \frac{F_0}{B} \right) \sin (\phi_Z + \phi_{B,r}) \sin (\phi_{B,p}) \cos \left[ 2\pi \left( \frac{F_0}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right] \right\} \\
= 4CB^3/2\frac{\partial F_0}{\partial \theta} R_T R_D \cos \left( 2\pi \frac{F_0}{B} \right) \cos (\phi_Z + \phi_{B,r}) \cos (\phi_{B,p}) \sin \left[ 2\pi \left( \frac{F_0}{B} - \frac{1}{2} \right) \pm \frac{\pi}{4} \right]. \tag{S2}
\]

Note that $\phi_{B,p}$ is constrained to an integer multiple of $\pi$, so that $\sin(\phi_{B,p}) = 0$.

IV. MAGNETIC BREAKDOWN

The interference of four individual oscillations results in the beating with the envelope function $\cos(2\pi \Delta F_0/B)$. We observe such a beating in the $\gamma$ oscillation. The magnetic field at the beating node $B_{\text{node}}$ is obtained by fitting the $\Delta \tau_0$ with Eq. (S2). Here, we omit $\partial F_r/\partial \theta$, $\cos(\phi_Z + \phi_{B,r})$, and $\cos(\phi_{B,p})$ factors since they are only related to the intensity and the sign. The so obtained $B_{\text{node}}$s are indicated by arrows in Fig. S2(a) together with the red fitting curves.

It is noticeable in Fig. S2(a) that $\Delta \tau_0$ for $\theta \geq 47.1^\circ$ have a finite intensity of oscillation even at $B = B_{\text{node}}$. Since $\Delta F_0/F_0$, $\sim 0.011$ is quite small, the difference of $\partial F_r/\partial \theta$ factor, the effective mass, or the Dingle temperature between the spin-split orbits may not account the intensity at $B_{\text{node}}$. A magnetic breakdown (MB) between the spin-split orbits is rather plausible origin because the intensity at $B_{\text{node}}$ becomes larger as $B_{\text{node}}$ increases with $\theta$. MB is an electron tunneling between two distinct extremal orbits at specific $k$ points. When an electron completes a closed orbit with an even number of MBs, it contributes to the dHvA oscillation whose frequency $F_{\text{MB}}$ corresponds to the area enclosed by its trajectory; $F_{\text{MB}}$ is between $F_0 \pm \Delta F_0$. Generally, the MB between spinless bands can occur when the cyclotron energy $h\omega_c = \hbar eB/m^* c$ exceeds $E_F^2/E_F$, where $E_F$ is an energy gap between the orbits and $E_F$ is the Fermi energy [14]. By using $E_F = 288$ meV and $m^*_c = 0.130 m_e$ at $\theta = 36.4^\circ$ and approximating $E_F$ as $2E_{\text{ASOI}} = 2.75$ meV obtained in the main manuscript, $B_c$ is estimated as $\sim 0.03$ T. The quite small $B_c$ indicates that the MB can occur when the spin polarization can be neglected.

In case of the MB between the spin-split bands, tunneling between the opposite spin state is expected to be suppressed [15]. This would be also the case of CaAgAs, where the energy scale of the spin-orbit interaction (SOI) $\Delta \sim 75$ meV is far larger than $\hbar eB/m^* c \sim 16$ meV at $B = 17.8$ T. An exception is at $k$ points where spin orient-
discrepancy between the orientation.

The spin polarization on the γ orbit for θ = 50° is shown in Fig. S2(b). There are five k points, indicated by circles, where spin polarization quickly changes; those are candidates of the breakdown k points where MB may occur. The observed MB oscillation is probably a sum of several MB oscillations corresponding to the MBs occurring at any possible selection of the breakdown k points. The intensity of the MB oscillation at $B = B_{\text{node}}$ decreases with θ and almost vanishes at θ = 42.1°. This trend may indicate that the MB only occurs at $B > B_{\text{c}} \sim 13$ T. The discrepancy between the $B_{\text{c}}$s estimated from the spinless assumption and the intensity at $B = B_{\text{node}}$ is probably because an electron needs to tunnel much longer distance (and larger $E_{\text{g}}$) than the spinless case to preserve the spin orientation.

The phase shift and the increase of $F_\gamma / B_{\text{node}}$ observed in $\Delta \tau_\gamma$ at θ ≥ 47.1° can also be explained by considering the effect of MB. The effect of MB can be introduced into Eq. (S2) as an additional factor $R_{m,n} = (ip)^m (q)^n$, where $p^2 + q^2 = 1$, $p^2$ ($q^2$) is the probability of (not) having MB at the breakdown k point, and $m$ ($n$) is the number of MBs (not) taking place at a breakdown k point in an orbit. Assuming that the probabilities of having a MB at each breakdown k points are equivalent, it is expressed as $p^2 = \exp(-B_{\text{c}}/B)$. Since our data is not sufficient to decompose the MB oscillations to each, we roughly approximate the MB oscillation as a single component which has a factor of $\alpha R_{2,3}$, a frequency of $F_{\text{MB}} = F_\gamma$, and an arbitrary phase shift $\phi_{\text{MB}}$. The $\alpha$ is a correction factor to take into account contributions from all MB oscillations. The phase shift occurs because the electron does not complete its orbit in a single band. Then, the MB oscillation for the γ orbit is expressed as

$$\Delta \tau_{\text{MB}} \approx 4 \alpha CB^{3/2} \frac{\partial F_\gamma}{\partial \theta} R_{T} R_{D} R_{2,3} \sin \left[ 2\pi \left( \frac{F_\gamma}{B} - \frac{1}{2} \right) - \frac{\pi}{4} + \phi_{\text{MB}} \right].$$

By taking a sum with the non-MB oscillation $\Delta \tau_\gamma$ multiplied by $R_{0.5}$, the total oscillation becomes

$$\Delta \tau_{\text{total}} = 4CB^{3/2} \frac{\partial F_\gamma}{\partial \theta} R_{T} R_{D}$$

$$(X^2 + Y^2)^{1/2} \sin \left[ 2\pi \left( \frac{F_\gamma}{B} - \frac{1}{2} \right) - \frac{\pi}{4} + \phi'_{\text{MB}} \right],$$

where

$$X = R_{0.5} \cos \left( 2\pi \frac{\Delta F_\gamma}{B} \right) \cos(\phi_Z + \phi_{\text{B},r}) \cos(\phi_{\text{B},p})$$

$$+ \alpha R_{2,3} \cos (\phi_{\text{MB}}),$$

$$Y = \alpha R_{2,3} \sin (\phi_{\text{MB}}),$$

$$\sin(\phi'_{\text{MB}}) = Y / \sqrt{X^2 + Y^2},$$

$$\cos(\phi'_{\text{MB}}) = X / \sqrt{X^2 + Y^2}.$$
FIG. S3. (a, b) Real spin polarization \( \mathbf{P} \) on the \( \beta \) orbit at (a) \( \theta = 0^\circ \) and (b) \( 45^\circ \). (c) The trajectories of \( \mathbf{P} \) along the \( \beta \) orbit at \( \theta = 0^\circ \) and \( 45^\circ \) projected on the Bloch sphere. (d) Angular dependence of the \( |\phi_{B,r}| \) for the \( \beta \) orbit.

a result, the \( \sigma_B \) in Eq. (2) is 0, and hence \( \phi_Z = 0 \). On the other hand, at \( \theta > 0^\circ \), \( B \) is no longer perpendicular to \( \mathbf{P} \). Thus, the increase of the \( \sigma_B \) is proportional to \( \sin \theta \) by approximating the \( \mathbf{P}(k) \) as being parallel to \( k_z \). Besides, \( \phi_Z \) is proportional not only to \( \sigma_B \) but also to \( m_3^* \), since \( v_{\perp} = \hbar k_{\perp}/m^* \). By approximating the \( \theta \) variation of the \( \beta \) orbit as the one of a cylinder along the \( k_z \)-axis, \( m_3^*(\theta) \) is expressed as \( m_3^*(0^\circ)/\cos \theta \). Therefore, the \( \phi_Z \) of the \( \beta \) roughly increases as \( \propto \tan \theta \).

VI. REAL SPIN BERRY PHASE OF THE \( \beta \) ORBIT

As mentioned in the main text, the \( \phi_{B,r} \) of the \( \beta \) orbit is constrained to integer-multiple of \( \pi \) only at \( \theta = 0^\circ \) by the \((0001)\) mirror operation, whereas it deviates from the constrained value at \( \theta > 0^\circ \). Here we show how the \( \phi_{B,r} \) is constrained at \( \theta = 0^\circ \) and how small the deviation of the \( \phi_{B,r} \) is at \( \theta > 0^\circ \) based on the \textit{ab initio} calculation.

Figure S3(a) shows the \( \mathbf{P} \) at \( k \) points on the \( \beta \) orbit at \( \theta = 0^\circ \). The \( \mathbf{P} \) is restricted within the \( k_y - k_z \) plane due to the \( D_{3h} \) point-group symmetry, as mentioned in Sec. V. Consequently, the trajectory of the \( \mathbf{P} \) along the \( \beta \) orbit projected on the Bloch sphere sweeps out zero solid angle, as shown in Fig. S3(c). As this solid angle directly corresponds to the twice of the Berry phase [17], the \( \phi_{B,r} \) of the \( \beta \) orbit at \( \theta = 0^\circ \) is zero.

In contrast, at \( \theta = 45^\circ \), the \( \mathbf{P} \) on the \( \beta \) orbit shown in Fig. S3(b) is not restricted within the \( k_y - k_z \) plane. Hence, the projected trajectory shown in Fig. S3(c) is deformed from the arc of \( \theta = 0^\circ \). However, the solid angle swept out by the trajectory is quite limited, and the corresponding \( \phi_{B,r} \) is as small as 0.02 \( \pi \). This is because the \( \beta \) orbit locates within the local \( k \)-space where \( \mathbf{P}(k) \) is a slowly varying function of \( k \), away from the vortex structure. Besides, the angular dependence of the \( \phi_{B,r} \) represented in Fig. S3(d) shows that the \( |\phi_{B,r}| \) monotonically increases from 0 as \( \theta \) varies from \( 0^\circ \). Therefore, neglecting the angular dependence of the \( \phi_{B,r} \) when analyzing the experimental data does not affect the result.

VII. SPIN-ZERO ANALYSIS ON THE \( \beta \) OSCILLATION

In the \( \beta \) orbit, the angular variation of the \( \phi_{B,r} \) is negligibly small (Sec. VI), whereas the \( \phi_Z \) increases in proportional to \( \tan \theta \) (Sec. V). Since we could not observe an apparent \( \beta \) oscillation at \( |\theta| < 17.1^\circ \), it is crucial to determine whether the \( \phi_Z \) changes the sign of \( \cos (\phi_Z + \phi_{B,r}) \) factor in Eq. (3) against \( \theta \). This is similar to the spin-zero analysis widely conducted on the (quasi-) 2D materials with spin-degeneracy (at \( B \to 0 \)) \textit{[18–21]}.

As seen in Fig. 4(d) in the main text, \( \Delta \tau_B \) does not change the sign against \( \theta \) between 17.1–47.1\(^\circ\). If there is a sign-change between \( 0^\circ \) and 17.1\(^\circ\), there should be another sign-change between 17.1\(^\circ\) and 47.1\(^\circ\) because \( \phi_Z \propto \tan \theta \) grows more rapidly as \( \theta \) increases. This fact indicates that the sign of \( \cos (\phi_Z + \phi_{B,r}) \) does not change in \( |\theta| \leq 47.1^\circ \).

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[1] E. Ohmichi and T. Osaka, Torque magnetometry in pulsed magnetic fields with use of a commercial microcantilever, Rev. Sci. Instrum. 73, 3022 (2002).

[2] P. Hohenberg and W. Kohn, Inhomogeneous Electron Gas, Phys. Rev. 136, B864 (1964).

[3] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carmonne, A. D. Corso, S. de Gironcoli, P. Dehugas, R. A. D. Jr., A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kamura, H.-Y. Ko, A. Kokalj, E. Küçükbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Poncé, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, Advanced capabilities for materials modelling with Quantum ESPRESSO, J. Phys.: Condens. Matter 29, 465901 (2017).

[4] J. P. Perdew, K. Burke, and M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77, 3865 (1996).

[5] G. Kresse and J. Furthmüller, Efficient iterative schemes for \textit{ab initio} total-energy calculations using a plane-wave basis set, Phys. Rev. B 54, 11169 (1996).

[6] J. Heyd, G. E. Scuseria, and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, J. Chem. Phys. 118, 8207 (2003).

[7] A. D. Corso, Pseudopotentials periodic table: From H to Pu, Comput. Mater. Sci. 95, 337 (2014).
[8] D. R. Hamann, Optimized norm-conserving Vanderbilt pseudopotentials, Phys. Rev. B 88, 085117 (2013).
[9] M. Schlipf and F. Gygi, Optimization algorithm for the generation of ONCV pseudopotentials, Comp. Phys. Commun. 196, 36 (2015).
[10] P. Scherpelz, M. Govoni, I. Hamada, and G. Galli, Implementation and Validation of Fully Relativistic GW Calculations: Spin–Orbit Coupling in Molecules, Nanocrystals, and Solids, J. Chem. Theory. Comput. 12, 3523 (2016).
[11] A. A. Mostofia, J. R. Yatesb, G. Pizzif, Y.-S. Leec, I. Souzad, D. Vanderbilte, and N. Marzari, An updated version of wannier90: A tool for obtaining maximally-localised Wannier functions, Comput. Phys. Commun. 185, 2309 (2014).
[12] P. M. C. Rourke and S. R. Julian, Numerical extraction of de Haas–van Alphen frequencies from calculated band energies, Comput. Phys. Commun. 183, 324 (2012).
[13] A. Alexandradinata, C. Wang, W. Duan, and L. Glazman, Revealing the Topology of Fermi-Surface Wave Functions from Magnetic Quantum Oscillations, Phys. Rev. X 8, 011027 (2018).
[14] D. Shoenberg, Magnetic Oscillations in Metals, Cambridge Monographs on Physics (Cambridge University Press, 1984).

[15] N. Kimura, H. Sano, M. Shirakawa, A. Ochiai, H. Funashima, and H. Harima, Orbital Crossing on Split Fermi Surfaces in Noncentrosymmetric Yb₄Sb₃, J. Phys. Soc. Jpn. 87, 114708 (2018).
[16] P. A. Frigeri, Superconductivity in crystals without an inversion center, Ph.D. thesis, ETH-Zürich (2005), original paper misprints a sign in the corresponding formula.
[17] D. Vanderbilt, Berry Phases in Electronic Structure Theory: Electric Polarization, Orbital Magnetization and Topological Insulators (Cambridge University Press, 2018) pp. 75–140.
[18] M. V. Kartsovnik, High magnetic fields: a tool for studying electronic properties of layered organic metals, Chem. Rev. 104, 5737 (2004).
[19] S. E. Sebastian, N. Harrison, and G. G. Lonzarich, Towards resolution of the Fermi surface in underdoped high-$T_c$ superconductors, Rep. Prog. Phys. 75, 102501 (2012).
[20] T. Terashima, H. T. Hirose, D. Graf, Y. Ma, G. Mu, T. Hu, K. Suzuki, S. Uji, and H. Ikeda, Fermi Surface with Dirac Fermions in CaFeAsF Determined via Quantum Oscillation Measurements, Phys. Rev. X 8, 011014 (2018).
[21] Y. Obata, Y. Kohama, S. Matsuishi, and H. Hosono, Shubnikovde Haas oscillations in the three-dimensional Dirac fermion system Ca₃PbO, Phys. Rev. B 99, 115133 (2019).