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**Nodal-line driven anomalous susceptibility in ZrSiS**

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We demonstrate a unique approach to test the signature of the nodal-line physics by thermodynamic methods. By measuring magnetic susceptibility in ZrSiS we found an intriguing temperature-driven crossover from dia- to paramagnetic behavior. We show that the anomalous behavior represents a real thermodynamic signature of the underlying nodal-line physics through the means of chemical pressure (isovalent substitution of Zr for Hf), quantum oscillations, and theoretical modeling. The anomalous part of the susceptibility is orbital by nature, and it arises due to the vicinity of the Fermi level to a degeneracy point created by the crossing of two nodal lines. Furthermore, an unexpected Lifshitz topological transition at the degeneracy point is revealed by tuning the Fermi level. The present findings in ZrSiS give an attractive starting point for various nodal-line physics-related phenomena to be tested by thermodynamic methods in other related materials.

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Dirac materials are characterized by a linear dispersion of energy-momentum curves near the Fermi energy. Due to the linearity of the dispersion, quasiarticles generically exhibit low effective masses and high mobilities [1]. Dirac states have been realized and studied in plenty of materials and new fascinating phenomena such as Fermi arcs and chiral anomalies have been revealed [2,3]. Under high-magnetic fields, these materials exhibit remarkably different behavior than conventional matter. The Landau levels become nonequidistant with a square root magnetic field dependence [4]. This feature is often used to verify the Dirac nature of a material experimentally [5,6].

The magnetic susceptibility, a low-field limit of the magnetic response function, in Dirac and nodal-line systems, shows unique properties due to the existence of band touching degeneracy points and/or lines [7–11]. For example, in contrast to ordinary metals, in Dirac materials the orbital (Landau) susceptibility diverges as the Fermi energy approaches the degeneracy point at low temperatures [7–10]. The orbital susceptibility originates from the dynamics of the Bloch electrons. It incorporates interband magnetic field mixing, and it is summed over Bloch states [12,13]. Although it possesses unique fingerprints, the susceptibility of novel Dirac systems has not been widely studied experimentally [14–16].

In this letter, we present a chemical pressure study of the magnetic susceptibility of the nodal-line Dirac semimetal ZrSiS. The susceptibility exhibits an anomalous temperature

dependence pointing towards a unique thermodynamic signature of nodal-line physics. The anomaly arises due to the Fermi level being located sufficiently close to the degeneracy point formed by the crossing of two nodal lines.

ZrSiS crystallizes in a tetragonal square-net crystal structure with nonsymmorphic  $P4/nmm$  (129) symmetry [17]. It is one of the reported topological nodal-line semimetals and has been the most extensively studied among a range of different nodal-line materials [18–26]. In ZrSiS, there are two types of nodal lines. Topologically protected nodal lines, nonsymmorphic symmetry protection, are positioned with about 1eV below the Fermi level and are not significant for our experimental findings [19,20]. However, close to the Fermi level, another set of nodal lines is found. Those nodal lines form a cage-like structure, see the inset to Fig. 1(c). They are not topologically protected, only  $C4v$  symmetry is present, and are thus prone to the opening of a gap that is induced by the spin-orbit (SO) interaction. Due to the relatively weak SO coupling, the resulting gap is small [27].

Angle-resolved-photoemission spectroscopy and high magnetic field studies together with first-principle calculations yield a reasonably well understood Fermi surface (FS) [22,25,28,29]. The FS is wrapped around the cagelike nodal lines. It consists of a pair of strongly anisotropic electron and hole pockets with open orbits along the  $k_z$  direction [22]. At the Fermi level only the Dirac-like bands are present, while the so-called “trivial” bands are well away [19].

Recent high-pressure studies reported a change in the Berry phase of the quantum oscillations (QOs), indicating the possibility of a topological phase transition (TPT). In Ref. [30]

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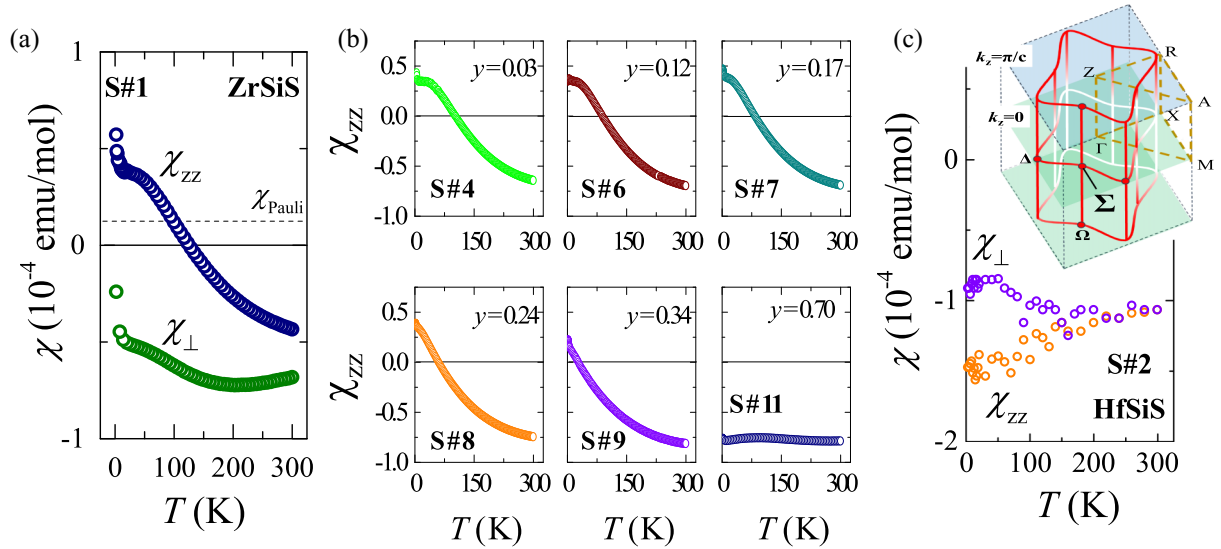


FIG. 1. Temperature ( $T$ ) dependent magnetic susceptibility of  $Zr_{1-y}Hf_ySiS$  taken at 1 T for various Hf concentrations  $y$ . (a) Out-of-plane  $\chi_{zz}$ , along [001], and in-plane  $\chi_{\perp}$  susceptibility of  $ZrSiS$ .  $\chi_{zz}$  has a strong anomalous  $T$  dependence with unexpected change in the susceptibility from diamagnetic at high  $T$  to paramagnetic at low  $T$ . By contrast  $\chi_{\perp}$  exhibits a weak  $T$  dependence with an impurity tail at low  $T$ .  $\chi_{Pauli}$  (dashed line) indicates the free-electron Pauli paramagnetic contribution as estimated from the specific heat measurements. (b)  $\chi_{zz}$  for different  $y$ : Upon increasing chemical pressure the sign change in  $\chi_{zz}$  shifts toward lower  $T$ . For  $y > 0.24$  the low- $T$  saturation of  $\chi_{zz}$  vanishes. At high doping  $y = 0.7$ ,  $\chi_{zz}$  flattens and remains diamagnetic in the whole  $T$  range examined. (c)  $\chi_{zz}$  and  $\chi_{\perp}$  for  $HfSiS$  exhibit a conventional, almost isotropic and weak  $T$  dependence. (Inset) Schematics of the cage of nodal lines in the 1st Brillouin zone. The intersecting nodal-line of interest  $\Sigma$  is located along the  $\Gamma$ - $M$  direction.

the authors report the possibility of a TPT at pressures as low as 0.5 GPa due to a phase change in the QO frequency mode  $F_{\delta_2}$ , this paper's notation. Additionally, the authors in Ref. [31] report another TPT at around 7 GPa with a transition detected in the QO frequency mode  $F_{\alpha}$ , again in the notation used here. In contrast, in our study, we observe a significantly different qualitative behavior, even in the low-chemical pressure limit, i.e., at low Hf concentrations ( $y$ ). We have detected two possible chemical-pressure-driven Lifshitz transitions in the low-frequency spectrum of the QOs. The first transition is associated with the emergence of a new frequency  $F_{\psi}$  around  $y = 0.24$ . The second transition is observed at around  $y \approx 0.34$  as indicated by the disappearance of the pocket  $F_{\delta_1}$ . The notable difference between the results of hydrostatic and chemical pressure could be traced back to a different compression of the crystal lattice: In the case of chemical substitution of Zr by Hf Vegard's law is obeyed, i.e., the tetragonal lattice ratio  $c/a = 2.273$  is practically constant across  $Zr_{1-y}Hf_ySiS$ , while that is not the case for the hydrostatic pressure where the ratio is reduced by increasing pressure [17,31].

Single crystals of  $Zr_{1-y}Hf_ySiS$  were grown by chemical vapor transport starting from a polycrystalline mixture of high-purity elements and iodine as a transport agent. With optimized growth conditions, well shaped prismatic crystals of several  $mm^3$  weighing 20–30 mg that are ideal for magnetization studies were observed. To get information on the concentration and homogeneity of the doped Hf atoms, the samples were characterized by employing an electron probe micro analysis and x-ray diffraction (XRD). XRD patterns show a systematic shift of the (002) peak upon increasing the

Hf concentration without any traces of segregation, indicating a homogeneous Zr-Hf solid solution.

Magnetic susceptibility ( $\chi$ ) vs temperature ( $T$ ) was measured using a Quantum Design MPMS superconducting quantum interference device magnetometer from 300 to 1.8 K in the linear response regime at a field of 1T. The out-of-plane susceptibility  $\chi_{zz}$  was measured along the [001] direction, and the in-plane susceptibility  $\chi_{\perp}$  was measured perpendicular to [001]. There was no difference in the sample response between field-cooled and zero-field-cooled measurements. The de Haas–van Alphen oscillations were measured in the [001] direction in the field range  $-7$  T to 7 T at several different temperatures in order to estimate the quasiparticle effective mass. The QOs were not significantly damped upon increasing the Hf concentration indicating a small level of atomic substitution-induced disorder.

Figure 1 summarizes magnetic susceptibility data of  $Zr_{1-y}Hf_ySiS$ . For  $y = 0$ , there is a strong anisotropy between  $\chi_{zz}$  and  $\chi_{\perp}$ , cf. Fig. 1(a). Moreover,  $\chi_{zz}$  has an unconventional steplike temperature dependence with a  $T$ -driven transition from a dia- to paramagnetic state and saturation towards the lowest  $T$ , whereas  $\chi_{\perp}$  is relatively weakly  $T$  dependent. The low- $T$  paramagnetism of  $ZrSiS$  is much stronger than expected for free-electron Pauli susceptibility term  $\chi_{Pauli}$  as derived from the specific heat density of states. The small upturns at the lowest temperatures (below  $\sim 10$ K) originate from paramagnetic impurities of 0.01%. On the other hand, the end compound  $HfSiS$  [Fig. 1(c)] exhibits more isotropic and  $T$ -independent susceptibility, which is more in line with expectations for conventional materials. To get better insight

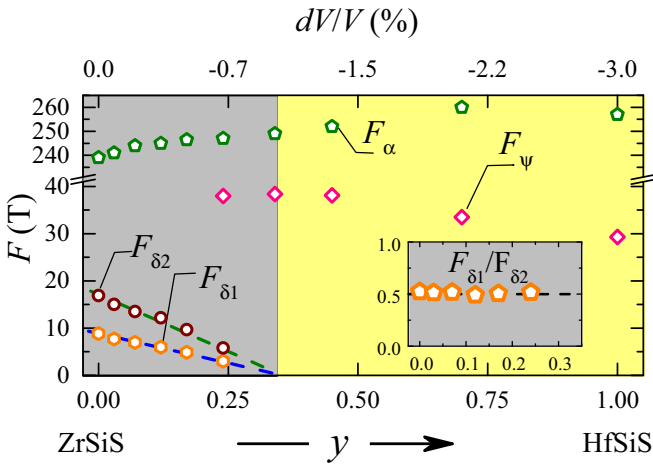


FIG. 2. Phase diagram of QO frequency vs Hf concentration  $y$  in  $\text{Zr}_{1-y}\text{Hf}_y\text{SiS}$  along the crystallographic [001] direction. Two Lifshitz transitions in the low-frequency spectrum are identified: A new pocket with frequency  $F_\psi$  emerges at around  $y = 0.24$ , and an electron pocket with frequency  $F_{\delta 1}$  ( $F_{\delta 2}$ ) vanishes at  $y \approx 0.34$  (as estimated from linear interpolations - green and blue dashed lines, respectively). Clearly, the low-frequency QOs seen in [001] direction for  $\text{ZrSiS}$  and  $\text{HfSiS}$  are topologically not connected. On the other hand the hole-pocket frequency  $F_\alpha$  increases with  $y$  and is continuously connected between  $y = 0$  and  $y = 1$ . The inset shows the ratio of the frequencies  $F_{\delta 1}/F_{\delta 2}$  which does not change with  $y$ . The dashed lines are guide to the eye.

into the unconventional behavior of  $\chi_{zz}(T)$  observed for  $y = 0$  we introduce positive chemical pressure by replacing Zr with isovalent Hf. Respective susceptibility measurements for selected  $y$  are shown in Fig. 1(b). Upon increasing the Hf content, the steplike feature indicative of the transition from dia- to paramagnetic behavior shifts to lower- $T$ . For  $y = 0.34$  the susceptibility starts to deviate from the steplike behavior, although the dia- to paramagnetic transition is still present. However, it is significantly weaker and no longer saturates towards low  $T$ , indicating that the effect responsible for this unconventional behavior is suppressed by chemical pressure. At  $y = 0.7$   $\chi_{zz}$  is  $T$  independent and remains diamagnetic.

To investigate whether the unconventional behavior of  $\chi_{zz}$  is linked to the change of the FS shape we have performed QO measurements for  $B \parallel [001]$ . Figure 2 shows the QO frequencies as a function of chemical pressure. It can be seen that the frequency  $F_\alpha$  associated with a hole-pocket orbit in the  $Z - R - A$  plane smoothly increases with  $y$ . On the other hand, in the low-frequency part of the diagram two Lifshitz transition can be identified. The first one is an ordinary  $2\frac{1}{2}$  [32] Lifshitz transition associated with the appearance of a new pocket with frequency  $F_\psi$ . It is detected at around  $y = 0.24$  and possibly could be ascribed to the appearance of an electron pocket at the  $\Gamma$  point as predicted by first-principles calculations in  $\text{HfSiS}$  [18].

The second Lifshitz transition is associated with the continuously traced disappearance of the oscillations with frequency  $F_{\delta 1}$  at around  $y = 0.3$ . As shown in the inset to Fig. 2, the ratio of  $F_{\delta 1}$  and  $F_{\delta 2}$  is constant and equal to 0.5. Thus we believe

$F_{\delta 2}$  originates from the second harmonic response of the QOs and is not indicative of an additional pocket. Interestingly, the disappearance of  $F_{\delta 1}$  coincides with the disappearance of the anomalous steplike behavior in the susceptibility: For  $y \leq 0.24$ , the value of the frequency  $F_{\delta 1}$  decreases with  $y$ . At the same time the sign change in  $\chi_{zz}$  from diamagnetic to paramagnetic shifts to lower  $T$  and for  $y = 0.34$   $F_{\delta 1}$  cannot be detected anymore, although  $\chi_{zz}(T)$  still exhibits a small sign change. However, the latter deviates considerably from the steplike behavior observed for smaller  $y$ .

$F_{\delta 1}$  seems to be produced by the FS cross section located near the  $\Sigma$  point [28,33], a degeneracy point at which the two nodal lines intersect [19,22], see Fig. 1(c). We can show that the observed temperature dependence of the magnetic susceptibility is also caused by the electron states in the vicinity of the  $\Sigma$  point. Neglecting the spin-orbit interaction, the dispersion of the two contacting bands “ $c$ ” and “ $v$ ” in the vicinity of this crossing point can be approximately described by the following expression [33,34]:

$$\varepsilon_{c,v}(\mathbf{k}) \approx B_2 k_2^2 + B_3 k_3^2 \pm [(v_F k_1)^2 + \beta^2 k_2^2 k_3^2]^{1/2}, \quad (1)$$

where  $v_F$ ,  $B_1$ ,  $B_2$ ,  $\beta$  are constant parameters of the spectrum, all the quasimomenta  $k_1$ ,  $k_2$ ,  $k_3$  are measured from the  $\Sigma$  point, and  $\varepsilon_{c,v}$  are measured from the energy of this point,  $\varepsilon_\Sigma$ . The  $k_1$  axis coincides with the twofold symmetry axis  $\Gamma$ -M along which the crossing point  $\Sigma$  is located. The  $k_2$  and  $k_3$  axes are along the tangents to the nodal lines crossing the  $\Sigma$  point (in particular, the  $k_3$  axis coincides with the  $z$  axis); see Fig. 1. According to Ref. [34], electron states in the vicinity of such a crossing point really can lead to an unusual anomaly in the magnetic susceptibility if the Fermi energy ( $E_F$ ) is close to  $\varepsilon_\Sigma$ . One has the following expression for the total magnetic susceptibility in this case [34,35]:

$$\chi_{zz} = \chi_0 + \Delta\chi [1 + \exp(-E_F/k_B T)]^{-1}, \quad (2)$$

where  $E_F$  is measured from the energy of the crossing point, and  $\chi_0$  is the magnetic susceptibility produced by the electron states lying far away from this point. The constant  $\Delta\chi$  is defined by the parameters of dispersion relation (1), and at  $|\lambda| \equiv 4|B_2 B_3|/\beta^2 \ll 1$ , it has the form [34,35]:

$$\Delta\chi \approx -4 \frac{e^2}{6\pi^2 \hbar c^2} \frac{v_F \beta}{B_3}, \quad (3)$$

where we have taken into account that in the case of  $\text{ZrSiS}$  four  $\Sigma$  points exist in the first Brillouin zone.

Formula Eq. (2) with the addition of a  $1/T$  term that is important below 10 K in order to account for the localized magnetic impurities reproduces the  $T$  behavior of  $\chi_{zz}$  extremely well in the low- $y$  region, Fig. 3(a), if the chemical potential  $E_F$  monotonically decreases with  $y$ , tending to the energy of the  $\Sigma$  point, Fig. 3(b). The parameter  $\Delta\chi$  remains practically constant with changing  $y$ , Fig. 3(d), which in the agreement with the natural assumption that the parameters  $v_F$ ,  $\beta$ , and  $B_3$  are constant or their variation is proportionally small to the small  $y$  [36].

For  $y > 0.3$ , formula (2) ceases to fit the experimental data. This failure of Eq. (2) at  $E_F \sim 10$  meV is due to the neglect of the spin-orbit interaction in deriving this formula. Note that the magneto-optical spectroscopy [27] shows that the gap in

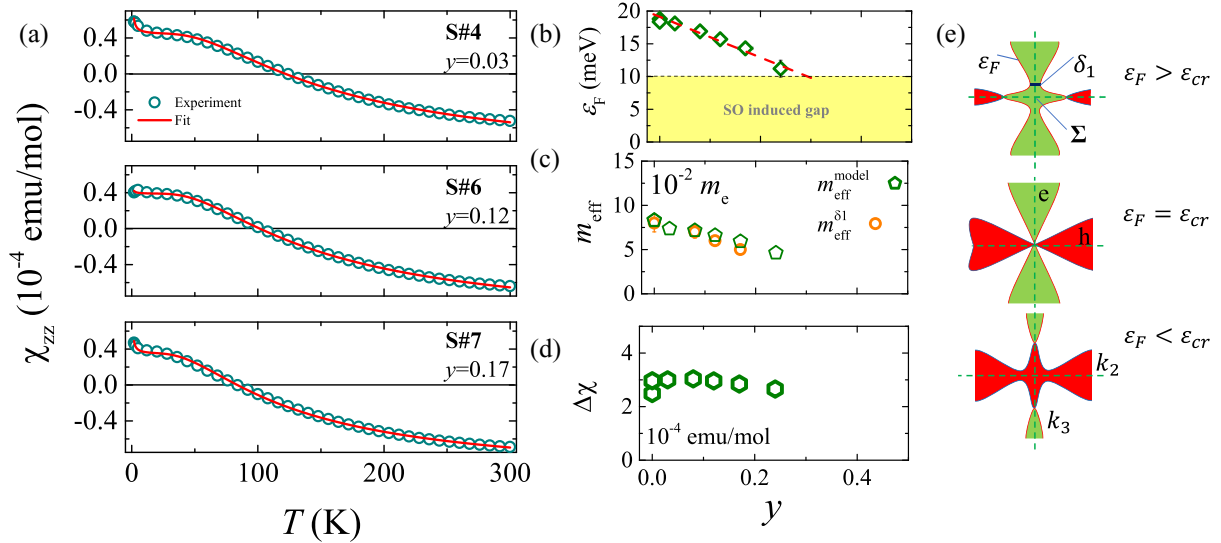


FIG. 3. (a) Fit of Eq. (2) to experimental  $\chi_{zz}(T)$  for samples  $y = 0.03, 0.12,$  and  $0.17$  including localized paramagnetic impurity contributions responsible for the low- $T$  upturn. The model fairly well captures the experimental data in the whole measured  $T$  range. (b) Fermi energy ( $E_F$ ) measured from the nodal-line crossing point as a function of  $y$ . Below  $\approx 10$  meV our model breaks down due to the SO-interaction induced gap at the nodal line. (c) Effective mass  $m_{\text{eff}}^{\delta_1}$  as estimated from QO of the  $\delta_1$  orbital compared with the effective mass  $m_{\text{eff}}^{\text{model}}$  as a function of  $y$ . (d) Almost constant value of  $\Delta\chi$  from Eq.(2) as a function of  $y$  indicates that the FS around the crossing points is not strongly modified for low levels of  $y$ . (e) Schematic drawing of the Fermi surface with self-intersecting orbitals near the degeneracy point  $\Sigma$  based on the model Eq.(1) (parameters  $B_1 = -B_2$  and  $\lambda < 0$ ). By tuning the Fermi energy the system undergoes a nonstandard Lifshitz transition characterized by a change in the configuration of the e-h pockets and direction of the intersecting orbitals.

the spectrum induced by this interaction is of the order of  $2\Delta \approx 26$  meV, and hence is comparable with the limiting value of  $E_F \sim 10$  meV. It is clear that at such a low value of  $E_F$ , one cannot neglect the spin-orbit gap.

Visible  $y$  correlation between  $F_{\delta_1}$  and the Fermi-level  $E_F$  extracted from the magnetic susceptibility indicate that the susceptibility and the frequency  $F_{\delta_1}$  are really determined by the same part of the FS near the  $\Sigma$  point. To support this conclusion quantitatively, in Fig. 3(c) we compare experimental QO effective masses with the one predicted by the model. The model predicts the effective mass of the cyclotron orbit around the neck of the electron tubelike pocket near the  $\Sigma$  to be  $m_{\text{eff}}^{\text{model}} = 3\hbar eF/2E_F$ , where  $F$  is the frequency of QOs of the neck orbitals, and  $E_F$  is the Fermi energy of the pocket [33]. Using the above-presented values yields effective masses that are in excellent agreement with those obtained from the QOs. The model can be further extended by taking into account a spectrum with the spin-orbit gap [37], suggesting that the gap does not exceed 10 meV. For  $y > 0.3$ ,  $E_F$  is likely located inside the spin-orbit gap at the  $\Sigma$  point, and so the gap effects become important. Indeed, if we check the FS shape obtained by the first-principles calculations for HfSiS we see a FS with nonoccupied states near the  $\Sigma$  point, see Ref. [38] and the Supplemental Material [39].

In conclusion, we present a comprehensive study of the anomalous magnetic susceptibility of ZrSiS, which arises due to the proximity of the Fermi energy to the degeneracy point formed by intersecting nodal lines. The anomalous sus-

ceptibility provides a rare opportunity to observe nodal-line physics by thermodynamic methods. Introduction of chemical pressure by replacing Zr with Hf in  $\text{Zr}_{1-y}\text{Hf}_y\text{SiS}$  allows one to trace the evolution of the susceptibility anomaly and to test the model of the electronic spectrum around the  $\Sigma$  degeneracy point. The model predicts a temperature-dependent orbital magnetization which is in excellent agreement with the experimental data for Hf concentrations  $y \leq 0.24$ . Also, the estimated spin-orbit gap at the nodal line matches the gap value obtained from the optical spectroscopy measurements. Moreover, the effective masses as estimated from quantum oscillations are in excellent agreement with those yielded within our theoretical model. The phase diagram of  $\text{Zr}_{1-y}\text{Hf}_y\text{SiS}$  reveals two different Lifshitz transitions, indicating a very rich topology-related physics which could also manifest in other closely related nodal-line systems [17,18].

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