Ideal inner nodal chain semimetals in Li$_2$XY (X = Ca, Ba; Y = Si, Ge) materials

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The chain-type nodal loops in the reciprocal space can generate exotic nodal chain fermions. Here, we report that Li$_2$XY (X = Ca, Ba; Y = Si, Ge) compounds are ideal inner nodal chain semimetals. Their band structures are composed of two connecting nodal loops with either hybrid or type-I band dispersion. The signatures of the nodal chain, such as the nontrivial surface states, are quite pronounced in these Li$_2$XY compounds since there is only a single inner nodal chain without other extraneous bands near the Fermi level. These compounds are existing materials and ambient-stable, which is available to realize the experimental detection of inner nodal chain fermions or further the practical applications.

Motivated by the discoveries of Weyl [1–5] and Dirac semimetals [6–10], topological semimetals currently attract significant research interests in condensed matter physics. Because of the existence of nontrivial band-crossings near the Fermi energy, topological semimetals can show exotic transport, magnetic and optical phenomena and great potential in electronics and quantum computing applications [11–15]. The band-crossings in topological semimetals can not only form zero-dimensional (0D) nodal points (including Weyl, Dirac and three-, six-, eight-fold degenerated nodal points [16]), but also can lead to one-dimensional (1D) nodal loop [17–19] and two-dimensional (2D) nodal surface [20–23]. Nodal loop semimetal has been proposed in many realistic materials so far [17–19, 24–39]. Many interesting properties including the drumhead surface state [17, 19], the anisotropic transport [40–43], the unconventional optical response [44, 45], and the potential surface magnetism and high-temperature superconductivity [46–49] were reported.

Compared with nodal point semimetal, nodal loop semimetal possess more variety of nodal structures. Such variety could be either from the dispersion around the band crossing or from its configuration. For the former, nodal loop is not limited to conventional type-I and type-II, but possesses the third occasion of the coexistence of type-I and type-II points in one loop (hybrid nodal loop). Hybrid nodal loop semimetal was notified recently [50–52], and only quite limited candidate materials were proposed [52]. Regarding the latter, nodal loop can take various configurations including a single loop, multiple crossing loops [53, 54], nodal chains [55–57], Hopf links [58–62], and etc. Nodal chain semimetal was initially proposed by Bzdušek et al. in IrF$_4$ materials [55], and by Yu et al. in HfC materials [63], along with anomalous magnetotransport properties. Later on, Chang et al. further classified nodal chain into outer and inner nodal chain, and predicted their coexistence in Heusler Co$_2$MnGa material [60]. Recently, the outer nodal chain state has been observed by Yan et al. in a metallic-mesh photonic crystal [64]. However, there is no experimental verification of an inner nodal chain semimetal yet, mostly because the electronic band structures of previous materials suffer from various drawbacks, such as the nodal chain situates away from the Fermi level, their exist other extraneous bands near the nodal chain, and so on. Therefore, ideal candidate materials are needed. As an ideal inner nodal chain semimetal, the candidate material needs to at least satisfy the following requirements. First, the nodal chain should be near the Fermi level. Second, the nodal chain needs to have a relatively simple shape, and it is the best that the system possesses a single chain composed of two, only two, closed loops. Third, it is crucial that near the nodal chain there is no extraneous bands, since the extraneous bands will strongly interferes with the unique physical properties related to the nodal chain semimetal. Fourth, the candidate materials should be stable and easy to be synthesized and facilitates the experimental studies. These rigorous conditions limit the development of suitable inner nodal chain candidates, and it is urgent to search for realistic materials that satisfy these requirements.

In current work, based on first-principles calculations and symmetry analysis, we propose that, a family of ambient-stable materials, lithium alkaline earth tetrildes Li$_2$XY (X = Ca, Ba; Y = Si, Ge), are ideal inner nodal chain semimetals that satisfy all the above mentioned requirements. Taking Li$_2$BaSi as a concrete example, we show that the material features a single inner nodal chain near the Fermi energy in the band structure. The nodal chain consists of two perpendicular closed nodal loops that situate in non-equivalent mirror/glide-mirror planes. Beside the two bands that form the nodal chain, there is no other extraneous bands nearby. As a result, clear drumhead surface states from the nodal chain are observed. More interestingly, we find that the two nodal loops of nodal chain in Li$_2$BaSi are both hybrid loops where type-I and type-II nodal points coexist. Therefore, our prediction provides ideal candidate materials for experimentally exploring the novel properties of inner nodal chain and hybrid nodal loop states.

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Noticing the three band-crossing points belong to k band-crossing points in Li\textsubscript{2} cause of the presence of both crossing-B on Γ-Y path, and crossing-C on Γ-Z path. Because of the presence of both P and T symmetries, the band-crossing points in Li\textsubscript{2}BaSi cannot be isolated [17]. Noticing the three band-crossing points belong to k\textsubscript{z}=0, k\textsubscript{y}=0 or k\textsubscript{z}=0 planes, we make a careful scan of band structures on these planes. As shown in Fig. 2(b), 2(c) and 2(d), we indeed find these points belong to two closed nodal loops centering the Γ point: one resides in k\textsubscript{y}=0 plane [denoted as NL1 in Fig. 2(c)] and the other situated in k\textsubscript{z}=0 plane [denoted as NL2 in Fig. 2(d)]. One also note that, there is no nodal loop in k\textsubscript{z}=0 plane [see Fig. 2(b)].

To further characterize the nodal loops, we construct a low-energy effective Hamiltonian around the Γ point. Given by the symmetry analysis, the conduction and valence bands in Li\textsubscript{2}BaSi correspond to irreducible representations B\textsubscript{2u} and B\textsubscript{3u} of the D\textsubscript{2h} symmetry, respectively. Taking them as basis states, the 2×2 effective Hamiltonian for the two bands around the Γ point takes the general form:

$$\mathcal{H} = \begin{bmatrix} M_1 + A_1 k_x^2 + B_1 k_y^2 + C_1 k_z^2 & D k_x k_y \\ D k_x k_y & M_2 + A_2 k_x^2 + B_2 k_y^2 + C_2 k_z^2 \end{bmatrix},$$

Here, the expansion is up to k-quadratic terms, and M\textsubscript{i}, A\textsubscript{i}, B\textsubscript{i} and C\textsubscript{i} with i=1,2, and D are material-specific coefficients. The Hamiltonian indicates that, a band-crossing point in k\textsubscript{x}=0 (and k\textsubscript{y}=0) plane will produce a nodal loop, which describes well the DFT results.

In fact, both nodal loops are protected by two independent symmetries when SOC is absent. One is the coexistence of P and T symmetries, which requests the Berry phase for any close path to be quantized in unit of π. We numerically calculated the Berry phase for each loop, the result give out to be ±π, ensuring the protection of them from opening gap against weak perturbations. The other protection is the glide-mirror symmetry g\textsubscript{y} (mirror symmetry m\textsubscript{x}) for NL1 (NL2). This requires the conduction and valence bands in Li\textsubscript{2}BaSi possess opposite g\textsubscript{y} (m\textsubscript{x}) eigenvalues in the glide-mirror (mirror) plane k\textsubscript{y}=0.
(kписываются тип-II), которые были подтверждены в наших DFT расчётах. 

Интересно, что два нодальных кольца не изолированы, но имеют контакт на пересечении -C, как показано на Fig. 2(e). Как уже упоминалось, структура нодального кольца может быть классифицирована в два типа (внешний нодальный цепь и внутренняя нодальная цепь) на основании конфигурации нодальных колец. В случае внешней нодальной цепи, две нодальные кольца расположены на противоположных сторонах касания, в то время как колца соприкасаются на внутренней нодальной цепи. Наконец, нодальная цепь в Li₂BaSi образует внутреннюю нодальную цепь структуры.

Нодальные кольца обычно проявляют козырьковые поверхности состояний [17]. В Li₂BaSi, два нодальных колца нодальной цепи находятся в плоскостях k_x=0 и k_z=0 соответственно. Таким образом, мы рассчитали спектры для обеих (010) и (100) поверхностей, как показано на Fig. 3(a) и 3(b). Более того, нодальные кольца в Li₂BaSi связаны с внутренней нодальной цепью. В случае внешней нодальной цепи, нодальные кольца в Li₂BaSi структура внутренней нодальной цепи.

После тщательного изучения спектра нодального состояния Li₂BaSi, как показано на Fig. 2(a), мы обнаружили, что нодальные колца в Li₂BaSi состоят из нодальных колец в Li₂BaSi. Внутренняя нодальная цепь имеет более низкое расположение нодальных точек, чем внешняя нодальная 

На нижнем и нижнем рисунках приведены увеличенные виды HSE06-спектр структуры нодального кольца для Li₂BaSi. Во всех рисунках показаны типы нодальных точек (A, B, и C). На рисунке (a) и (b) видно, что транспортная способность нодального кольца в Li₂BaSi отличается от других материалов. Например, в Li₂BaSi, нодальные кольца в Li₂BaSi состоят из нодальных колец в Li₂BaSi. Внутренняя нодальная цепь имеет более низкую частоту нодальных точек, чем внешняя нодальная цепь. В Li₂BaSi, нодальные кольца в Li₂BaSi состоят из нодальных колец в Li₂BaSi. Внутренняя нодальная цепь имеет более низкую частоту нодальных точек, чем внешняя нодальная цепь. В Li₂BaSi, нодальные кольца в Li₂BaSi состоят из нодальных колец в Li₂BaSi. Внутренняя нодальная цепь имеет более низкую частоту нодальных точек, чем внешняя нодальная цепь. В Li₂BaSi, нодальные кольца в Li₂BaSi состоят из нодальных колец в Li₂BaSi. Внутренняя нодальная цепь имеет более низкую частоту нодальных точек, чем внешняя нодальная цепь.
under the protection of two independent mechanism (either PT symmetry or mirror/glide-mirror symmetry). An effective Hamiltonian is constructed to describe the nodal chain. Moreover, we find the nodal chain in these materials makes up either from hybrid or type-I nodal loops. This family of materials are stable and quite easy to synthesize, which further make them as suitable candidate materials to investigate the interesting physics associated with nodal chain, as well as type-I and hybrid nodal loops.

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[1] X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, Phys. Rev. B 83, 205101 (2011).
[2] S. Morakami, New J. Phys. 9, 356 (2007).
[3] A. A. Burkov and L. Balents, Phys. Rev. Lett. 107, 127205 (2011).
[4] H. Weng, C. Fang, Z. Fang, B. A. Bernevig, and X. Dai, Phys. Rev. X 5, 011029 (2015).
[5] S. M. Huang, S. Y. Xu, I. Belopolski, C. C. Lee, G. Chang, B. K. Wang, N. Alidoust, G. Bian, M. Neupane, C. Zhang, S. Jia, A. Bansil, H. Lin, and M. Z. Hasan, Nat. Commun. 6, 7373 (2014).
[6] S. M. Young, S. Zaheer, J. C. Y. Teo, C. L. Kane, E. J. Mele, and A. M. Rappe, Phys. Rev. Lett. 108, 140405 (2012).
[7] Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, and Z. Fang, Phys. Rev. B 85, 195320 (2012).
[8] Z. Wang, H. Weng, Q. Wu, X. Dai, and Z. Fang, Phys. Rev. B 88, 125427 (2013).
[9] B.-J. Yang and N. Nagaosa, Nat. Commun. 5, 4898 (2014).
[10] S. Borisenko, Q. Gibson, D. Evtushinsky, V. Zabolotnyy, B. Bhemer, and R. J. Cava, Phys. Rev. Lett. 113, 027603 (2014).
[11] M. Koshino and T. Ando, Phys. Rev. B 81, 195431 (2010).
[12] A. A. Zyuzin and A. A. Burkov, Phys. Rev. B 86, 115133 (2012).
[13] A. A. Zyuzin, S. Wu, and A. A. Burkov, Phys. Rev. B 85, 165110 (2012).
[14] P. Hosur and X. Qi, C. R. Phys. 14, 857 (2013).
[15] K. Fukushima, D. E. Kharzeev, and H. J. Warringa, Phys. Rev. D 78, 074033 (2008).
[16] B. Bradlyn, J. Cano, Z. Wang, M. G. Vergniory, C. Felser, R. J. Cava, and B. A. Bernevig, Science 353, 3533, eaaf5037 (2016).
[17] H. Weng, Y. Liang, Q. Xu, R. Yu, Z. Fang, X. Dai, and Y. Kawazoe, Phys. Rev. B 92, 045108 (2015).
[18] S. A. Yang, H. Pan, and F. Zhang, Phys. Rev. Lett. 113, 046401 (2014).
[19] Y. Chen, Y. Xie, S. A. Yang, H. Pan, F. Zhang, M. L. Cohen, and S. Zhang, Nano Lett. 15, 6974 (2015).
[20] C. Zhong, Y. Chen, Y. Xie, S. A. Yang, M. L. Cohen, and S. B. Zhang, Nanoscale 8, 7232 (2016).
[21] Q.-F. Liang, J. Zhou, R. Yu, Z. Wang, H. Weng, Phys. Rev. B 93, 085427 (2016).
[22] W. Wu, Y. Liu, S. Li, C. Zhong, Z. Yu, X. Sheng, Y. Zhao, and S. Yang, Phys. Rev. B 97, 115125 (2018).
[23] X. M. Zhang, Z.-M. Yu, Z. M. Zhu, W. K. Wu, S.-S. Wang, X.-L. Sheng, and S. A. Yang, arXiv:1805.01614.
[24] Y. Kim, B. J. Wieder, C. L. Kane, and A. M. Rappe, Phys. Rev. Lett. 115, 036806 (2015).
[25] R. Yu, H. Weng, Z. Fang, X. Dai, and X. Hu, Phys. Rev. Lett. 115, 036807 (2015).
[26] L. S. Xie, L. M. Schoop, E. M. Seibel, Q. D. Gibson, W. Xie, and R. J. Cava, APL Mater. 3, 083602 (2015).
[27] Y. Chen, Y.-M. Lu, and H.-Y. Kee, Nat. Commun. 6, 6593 (2015).
[28] R. H. Li, H. Ma, X. Cheng, S. Wang, D. Li, Z. Zhang, Y. Li, and X.-Q. Chen, Phys. Rev. Lett. 117, 096401 (2016).
[29] 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, Nat. Commun. 7, 10556 (2016).
[30] C. Fang, H. Weng, X. Dai, and Z. Fang, Chin. Phys. B 25, 117106 (2016).
[31] L.-Y. Gan, R. Wang, Y. J. Jin, D. B. Ling, J. Z. Zhao, W. P. Xu, J. F. Liu, and H. Xue, Phys. Chem. Chem. Phys. 19, 8210 (2017).
[32] X. Zhang, Z.-M. Yu, X.-L. Sheng, H. Y. Yang, and S. A. Yang, Phys. Rev. B 95, 235116 (2017).
[33] S. Li, Y. Liu, S.-S. Wang, Z.-M. Yu, S. Guan, X.-L. Sheng, Y. G. Yao, and S. A. Yang, Phys. Rev. B 97, 045131 (2018).
[34] R. Yu, Q. Wu, Z. Fang, and H. Weng, Phys. Rev. Lett. 119, 036401 (2017).
[35] S. Li, Z.-M. Yu, Y. Liu, S. Guan, S.-S. Wang, X. Zhang, Y. Yao, and S. A. Yang, Phys. Rev. B 96, 081106(R) (2017).
[36] X. M. Zhang, L. Jin, X. F. Dai, and G. D. Liu, J. Phys. Chem. Lett. 8, 4814 (2017).
[37] T.-T. Zhang, Z.-M. Yu, W. Guo, D. Shi, G. Zhang, and Y. Yao, J. Phys. Chem. Lett. 8, 5792 (2017).
[38] C. Chen, S.-S. Wang, L. Liu, Z.-M. Yu, X.-L. Sheng, Z. Chen, and S. A. Yang, Phys. Rev. Mater. 1, 044201 (2017).
[39] X. M. Zhang, L. Jin, F. X. Dai, and G. D. Liu, Appl. Phys. Lett. 112, 122403 (2018).
[40] R. Singha, A. Parihari, B. Satpati, and P. Mandal, Proc. Natl. Acad. Sci. USA 114, 2468 (2017).
[41] M. N. Ali, L. M. Schoop, C. Garg, J. M. Lippmann, E. Lara, B. Lotsch, and S. Parkin, arXiv:1603.09318.
[42] X. Wang, X. Pan, M. Gao, J. Yu, J. Jiang, J. Zhang, H. Zuo, M. Zhang, Z. Wei, W. Niu, Z. Xia, X. Wan, Y. Chen, F. Song, Y. Xu, B. Wang, G. Wang, and R. Zhang, Adv. Electron. Mater. 2, 1600228 (2016).
[43] J. Hu, Z. Tang, J. Liu, X. Liu, Y. Zhu, D. Graf, Y. Shi, S. Che, C. N. Lau, J. Wei, and Z. Mao, Phys. Rev. Lett.
[44] S. Guan, Z.-M. Yu, Y. Liu, G.-B. Liu, L. Dong, Y. Lu, Y. Yao, and S. A. Yang, npj Quantum Mater. 2, 23 (2017).
[45] Y. Liu, Z.-M. Yu, and S. A. Yang, Phys. Rev. B 96(R), 121101 (2017).
[46] C.-L. Zhang, Z. Yuan, G. Bian, S.-Y. Xu, X. Zhang, M. Z. Hasan, and S. Jia, Phys. Rev. B 93, 054520 (2016).
[47] T.-R. Chang, P.-J. Chen, G. Bian, S.-M. Huang, H. Zheng, T. Neupert, R. Sankar, S.-Y. Xu, I. Belopolski, G. Chang, B. Wang, F. Chou, A. Bansil, H.-T. Jeng, H. Lin, and M. Z. Hasan, Phys. Rev. B 93, 245130 (2016).
[48] G. M. Pang, M. Smidman, L. X. Zhao, Y. F. Wang, Z. F. Weng, L. Q. Che, Y. Chen, X. Lu, G. F. Chen, and H. Q. Yuan, Phys. Rev. B 93, 060506 (2016).
[49] S.-Y. Guan, P.-J. Chen, M.-W. Chu, R. Sankar, F. Chou, H.-T. Jeng, C.-S. Chang, and T.-M. Chuang, Science Advances 2, e1600894 (2016).
[50] Y. Gao, Y. Chen, Y. Xie, P. Chang, M. L. Cohen, and S. Zhang, arXiv:1707.04576.
[51] R. Chen, B. Zhou, and D.-H. Xu, arXiv:1801.01683.
[52] X. M. Zhang, Z.-M. Yu, Y. H., Lu, X.-L. Sheng, H. Y. Yang, and S. A. Yang, Phys. Rev. B 97, 125143 (2018).
[53] Y. Du, F. Tang, D. Wang, L. Sheng, E.-J. Kan, C.-G. Duan, S. Y. Savrasov, and X. Wan, npj Quantum Mater. 2, 3 (2017).
[54] S. Kobayashi, Y. Yamakawa, A. Yamakage, T. Inohara, Y. Okamoto, and Y. Tanaka, Phys. Rev. B 95, 245208 (2017).
[55] T. Bzdusek, Q. S. Wu, A. Regg, M. Sigrist, and A. A. Soluyanov, Nature (London) 538, 75 (2016).
[56] X.-L. Sheng, Z.-M. Yu, R. Yu, H. Weng, and S. A. Yang, J. Phys. Chem. Lett. 8, 3506 (2017).
[57] S.-S. Wang, Y. Liu, Z.-M. Yu, X.-L. Sheng, and S. A. Yang, Nat. Commun. 8, 1844 (2017).
[58] C. Zhong, Y. Chen, Z.-M. Yu, Y. Xie, H. Wang, S. A. Yang, and S. Zhang, Nat. Commun. 8, 15641 (2017).
[59] W. Chen, H.-Z. Lu, and J.-M. Hou, Phys. Rev. B 96, 041102 (2017).
[60] G. Chang, S.-Y. Xu, X. Zhou, S.-M. Huang, B. Singh, B. Wang, I. Belopolski, J. Yin, S. Zhang, A. Bansil, H. Lin, and M. Z. Hasan, Phys. Rev. Lett. 119, 156401 (2017).
[61] Z. Yan, R. Bi, H. Shen, L. Lu, S.-C. Zhang, and Z. Wang, Phys. Rev. B 96, 041103 (2017).
[62] P.-Y. Chang and C.-H. Yee, Phys. Rev. B 96, 081114 (2017).
[63] R. Yu, Q. S. Wu, Z. Fang, and H. M. Weng, Phys. Rev. Lett. 119, 036401 (2017).
[64] Q. Yan, R. Liu, Z. Yan, B. Liu, H. Chen, Z. Wang, and L. Lu, Nat. Phys. 14, 461 (2018).
[65] H. Axel, W. Muller, H. Schafer, and A. Weiss, Z. Naturforsch. 22b, 1081 (1967).
[66] D. Stoiber, M. Bobnar, P. Hohn, and R. Niewa, Z. Naturforsch. 72(11), 847 (2017).
[67] See Supplemental Material for computational methods, the optimized atomic positions of Li\textsubscript{2}XY compounds, the schematic illustrations of inner nodal chain, crossing nodal loops, and outer nodal chain, the band structures of Li\textsubscript{2}CaSi and Li\textsubscript{2}CaGe without SOC; the band structures of Li\textsubscript{2}BaSi and Li\textsubscript{2}CaSi under SOC.