Electronic Properties of the Weyl Semimetals Co$_2$MnX (X=Si, Ge, Sn)

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Using first-principles electronic structure calculations, it is shown that ferromagnetic Heusler compounds Co$_2$MnX (X = Si, Ge, Sn) present nontrivial topological characteristics and belong to the category of Weyl semimetals. These materials exhibit two topologically interesting band crossings near the Fermi level. These band crossings have complex 3D geometries in the Brillouin zone and are characterized by nontrivial topology as Hopf links and chain-like nodal lines that are protected by the perpendicular mirror planes. The spin–orbit interaction split these nodal lines into several 0D Weyl band crossings. Unlike previously known topologically nontrivial Heusler materials, these majority spin band crossings lie in or very near to the bandgap of minority spin bands, potentially facilitating experimental observation.

1. Introduction

Since the discovery of Weyl semimetallic behavior in TaAs,[1–4] several topological semimetals have been predicted, including nodal-line semimetals,[5,6] Z$_2$-topological semimetals,[7–9] non-symmorphic nodal-chain metals,[10] Kramers Weyl fermions,[11] and magnetic Dirac semimetals.[12–14] Topological semimetals can further be classified and characterized by the dimensionality of band crossings in the bulk Brillouin zone (BZ).[15] In Dirac or Weyl semimetals, conduction and valence bands cross at discrete points in the BZ, i.e., at 0D crossings. For nodal-line semimetals, the band crossings follow a line in the BZ and hence, they are 1D. These band crossing may follow complex geometries in the 3D BZ. Topological phase transitions between different types of topological semimetals have also been shown.[16]

Heusler compounds host a variety of nontrivial topological phases, including topological insulators (TI) and Weyl semimetals (WSM). In general, they offer high tunability of electronic properties, owing to the stability of a wide range of chemical combinations in different sites of their crystal structure.[17] Rare-earth half-Heusler compounds PtLuBi (Ln = Y, La, and Lu) were one of the first topological materials predicted based on electronic structure calculations, with large spin–orbit coupling and strong band inversion,[18–20] and later experimentally verified for PtLuBi, PtYBi,[21] and PtLuSb.[22] Hopf-link semimetallic phases have been predicted in magnetic Co$_2$TiX (X = Si, Ge, and Sn) and Co$_2$MnGa full-Heuslers.[23,24] Slight changes in chemical compositions may lead to significant modifications in their electronic structure, potentially resulting in novel topological phases.

In this work, we investigate nontrivial topological features in the full-Heusler compounds Co$_2$MnX (X = Si, Ge, and Sn). These materials are ferromagnetic with high Curie temperatures.[25,26] The majority spin bands near the Fermi level exhibit several 3D band crossings in the bulk BZ. Some of these band crossings, which are protected by different crystal symmetries, are entangled and are classified as Hopf links.[25] Upon breaking time reversal symmetry, these band crossings split up into several 0D crossings called Weyl nodes. These Weyl nodes exhibit topologically nontrivial characteristics that may be easier to probe experimentally due to the half-metallic character of these materials.

2. Computational Approach

The calculations are based on the generalized Koh–Sham theory[27,28] with generalized gradient approximation of Perdew–Burke–Ernzerhof revised for solids (PBEsol),[29] as implemented in the VASP code.[30,31] The interaction between the valence electrons and the ionic cores are treated using projector augmented wave potentials.[32,33] The calculations are
performed using a primitive cell of four atoms, with 350 eV energy cutoff for the plane-wave expansion and 16 × 16 × 16 Γ-centered mesh of k points for integrations over the BZ. Tight-binding calculations are performed using the Wannier90 code,[34] with Hamiltonian extracted from the density functional theory calculations. Topological features of the band structure are computed with the tight-binding Hamiltonian using the WannierTools code.[35]

3. Results and Discussion

3.1. Crystal Symmetry of Co2MnX (X = Si, Ge, Sn)

The full-Heusler crystal structure of Co2MnX (X = Si, Ge, or Sn), space group Fm3m, is composed of four interpenetrating face-centered cubic sublattices, as shown in Figure 1a. The corresponding BZ is shown in Figure 1b. The calculated lattice parameters of Co2MnSi, Co2MnGe, and Co2MnSn are 5.56, 5.65, and 5.90 Å, which are in good agreement with the experimental values 5.66,[36] 5.75,[36] and 5.976 Å[37] respectively. The crystal structure has space inversion symmetry, with nine mirror-symmetry planes, Mx(x = 0), My(y = 0), Mz(z = 0), Mx(y = y), My(z = z), Mz(x = -z), Mx(z = -y), My(x = -z), and My(z = y = y). These symmetry planes play important role in the topological property of these materials, as discussed in the subsequent sections.

3.2. Electronic Band Structure of Co2MnX (X = Si, Ge, and Sn)

Co2MnSi and Co2MnGe have been characterized as half-metallic ferromagnets with magnetization M = 5\mu_B per formula unit and Curie temperatures greater than 900 K.[36] These materials have 29 valence electrons per formula unit (Nv = 29) and satisfy the Slater Pauling rule[38] according to which M = Nv - 24. The spin-polarized electronic band structure of Co2MnSi, Co2MnGe, and Co2MnSn without the effect of spin–orbit interaction is shown in Figure 2. Here, we find that Co2MnSi is a half-metal with sizable gap of 0.72 eV in the minority spin channel (Figure 2a), in agreement with previous electronic structure calculations[39,40] and photoemission experiments.[41] In the case of Co2MnGe and Co2MnSn, our calculations show that they are on the brink of becoming half-metals, with the Fermi level only touching the top of the valence band in the minority spin channel of Co2MnGe (Figure 2b), with a bandgap of 0.35 eV in agreement with previous calculations.[42] We note that recent angle-resolved photoemission spectrosocpy (ARPES) measurements in Co2MnGe find the Fermi level at less than 0.1 eV above the top of the valence band in the minority spin gap,[43] in overall good agreement with our calculations. However, we note that ARPES is highly surface sensitive, and previous measurements on Co2MnSi indicate a strong dependence of the Fermi-level position on the surface termination.[44] For Co2MnSn, the Fermi level is slightly below the top of the valence band (with a small bandgap of 0.18 eV) leading to a very small, yet non zero, minority spin density of states at the Fermi level (Figure 2c), also in agreement with previous calculations.[42]

Regarding the topological features, there are two interesting band crossings in the majority spin band structure near the Fermi level as highlighted in the top panel of Figure 2. The topology of these band crossing is dependent on the symmetry of the system. The evolution of these band crossings across the BZ with and without the inclusion of spin–orbit interaction will be discussed in the next few sections. It is worth noting that here different from previously explored Co2MnGa,[24] the half-metal-like behavior of Co2MnX (X = Si, Ge, and Sn), with very small minority spin density of states in the Ge- and Sn-based compounds, may facilitate the experimental observations of Weyl nodes, for example, by spin-resolved transport or spin-resolved ARPES. As the nature of the band crossings in the majority spin channel is the same in these three compounds, as shown in Figure 2, we opt to focus the discussion on the case of Co2MnGe. The conclusions for the other two materials are similar.

3.3. Nodal Lines in Co2MnGe

The two topologically interesting band crossings near the Fermi level in the majority spin band structure are indicated in Figure 2a–c. To understand the geometry of these band crossings in the 3D BZ, without the inclusion of spin–orbit coupling, we track them separately. Figure 3a shows the majority spin band structure of Co2MnGe without the effect of spin–orbit interaction, obtained from a Wannier-based tight-binding (TB) model. The TB hopping parameters are extracted from first-principles calculations, which present very good agreement with DFT band
structure. The bands containing the lower band crossing is highlighted in Figure 3a. To track the crossing between the two bands containing the lower band crossing, we have calculated the energy gap separation of the pair of bands for each \( k \)-point, \( \Delta(\tilde{k}) = E_n(\tilde{k}) - E_{n-1}(\tilde{k}) \), along different mirror symmetry planes. For the lower band crossing in the majority spin, Figure 2b, we populate the band indicated by the arrow in Figure 3a and find the gap between this highest occupied and the next lowest unoccupied band (shaded region in Figure 3a). The projection of the gap between these two bands is shown in Figure 3b–d along \( k_z = 2\pi/a \), \( k_x = k_y \), and \( k_z = 0 \) plane, which are also mirror symmetry planes as discussed in Section 3.1.

There are three different types of nodal lines that can be observed here. The dispersion of these nodal lines in the BZ is shown in Figure 3e–g. The pink and orange nodal lines are protected by \( M_x \), \( M_y \), and \( M_z \) mirror planes, while blue nodal lines are protected by \( M_{xy} \), \( M_{xz} \), and \( M_{yz} \) mirror planes. Interestingly, all these three types of nodal lines are entangled, forming a nodal chain, as shown in Figure 4, where all the nodal lines corresponding to the lower band crossing are plotted together. Two nodal lines (in orange) are interlinked as shown in Figure 3g and 4, forming a Hopf link. Each nodal line in pink is connected to four orange nodal lines and four blue nodal lines. The trajectory of these nodal lines in the BZ, protected by different mirror symmetries, gives rise to another category of topological semimetals. Similar network of nodal lines has also been found in \( \text{Co}_2\text{MnGa} \), due to similarity in the nature of associated bands.

Next, we track the upper band crossing near the Fermi level, along the \( W \)–\( K \) direction, of the majority-spin band structure shown in Figure 2b, using a similar approach as described above. The bands containing the upper band crossing are highlighted in Figure 5a. The bands up to the highlighted band in Figure 5a are occupied and the gap between this highest occupied and lowest unoccupied band is computed and projected along different mirror symmetry planes. Unlike the case above, we observe that these bands cross along \( k_x = 0 \), \( k_y = 0 \), and \( k_z = 0 \) symmetry planes. The projection of the gap in \( k_z = 0 \) is shown in Figure 5b,c. The dispersion of this nodal line in the BZ is shown in Figure 5d. This kind of nodal lines is also seen in the Heusler Weyl semimetals \( \text{Co}_2\text{TiX} \) (\( X = \text{Si}, \text{Ge}, \text{Sn} \)). However, \( \text{Co}_2\text{TiX} \) only contains one band-crossing near the Fermi level. In contrast, in the family of Weyl semimetals \( \text{Co}_2\text{MnX} \) (\( X = \text{Si}, \text{Ge}, \text{Sn} \)) discussed here, there are two topologically interesting band crossings near the Fermi level. This may lead to significant differences in the experimental observables such as Fermi arc surface states and anomalous Hall conductivity (AHC).

3.4. Effects of Spin–Orbit Coupling on the Electronic Structure of \( \text{Co}_2\text{MnGe} \)

Here, we analyze the effects of spin–orbit interaction on the band structure of \( \text{Co}_2\text{MnX} \) (\( X = \text{Si}, \text{Ge}, \text{Sn} \)), again taking \( \text{Co}_2\text{MnGe} \) as example. As these materials are ferromagnetic, the symmetry of the system and electronic properties will depend on the magnetization direction. We calculate the
magnetic anisotropy energy for magnetization along [001], [110], and [111] directions. The energy of the system along these three magnetization directions is very similar, differing by less than 0.1 meV per formula unit. After inclusion of spin–orbit interaction, mirror symmetry is broken along certain planes. Consequently, 1D nodal lines along those planes split up into 0D nodes. For instance, if magnetization is along [001] direction, the $M_z(k_z = 0)$ mirror symmetry is preserved, while along other mirror planes is broken. As a result, the nodal line along $k_z = 0$ is preserved, while nodal lines along the other mirror planes are gapped as the respective mirror symmetry is broken, resulting in the emergence of Weyl nodes. Due to the small magnetization anisotropy energy, the magnetic orientation can be tuned by an external field, and thus the formation and location of the Weyl nodes can be controlled.[23,24]

Figure 3. Tight-binding band structure Co$_2$MnGe. a) Majority spin band structure with the shaded region indicating the gap between the highest occupied and lowest unoccupied band. Projection of the energy gap, $\Delta(k)$, between highest occupied and lowest unoccupied band on different planes, b) $k_z = 1$ plane, c) $k_x = k_y$ plane, and d) $k_z = 0$, showing three different types of nodal lines. e-g) The location of the nodal lines in the 3D BZ is shown in (e), (f), and (g).

Figure 4. Connection of the different nodal lines from Figure 3e–g, in the 3D BZ of Co$_2$MnGe.
Figure 5. Band structure of Co$_2$MnGe highlighting the higher band crossing near the Fermi level. a) Majority spin band structure with the arrow indicating highest occupied band in the TB model. b) The gap ($\Delta(k)$) between the highest occupied and lowest unoccupied bands (shaded region in (a)) projected on the $k_z = 0$ plane. c) The nodal line shown in $k_x - k_y$ plane. d) The dispersion of this nodal line in 3D BZ.

Figure 6. a) Atomic projected electronic structure of Co$_2$MnGe in the presence of spin–orbit coupling and magnetization along [111] direction. b,c) The band crossings discussed in this section are highlighted by red and brown circles and enlarged in (b) and (c).
where $\Omega_n^\alpha$ is the Berry curvature for band $n$, $\hat{v}_{\alpha} = \frac{\hbar}{\epsilon} \frac{\partial \hat{H}}{\partial k}$ is the velocity operator for $\alpha, \beta, \gamma = x, y, z$, and $|u_n(k)\rangle$ and $E_n(k)$ are the eigenvectors and eigenvalues of the Hamiltonian $\hat{H}(k)$, respectively. For the computation of Berry curvature, we have taken the summation in $\Omega_n^\alpha$ over all bands up to the lower band crossing (brown circle in Figure 6a). The plot of Berry curvature in $k_y = 0$ plane is shown in Figure 7. Several discontinuities are observed in the plot of Berry curvature along the $k_y = 0$ plane, where Weyl nodes appear. High positive (negative) spikes in the values of Berry curvature are associated with the Weyl nodes of positive (negative) chirality, representing the source (sink) of Berry curvature. Several pairs of Weyl nodes also appear along other symmetry planes. The separation between Weyl nodes of opposite chirality in momentum space is very small ($\approx 0.02$ in units of $2\pi/\alpha$). Moreover, our calculations show that there is significant mixing of trivial surface states near the Fermi level, with the topologically protected Fermi arc states, which makes it very challenging to distinguish between Weyl nodes of opposite chirality in momentum space. A range of AHC values are observed in the plot of Berry curvature along the $k_y = 0$ plane. Where Weyl nodes are present, the Fermi arc states make it very challenging to distinguish between trivial surface states and Fermi arc states.

Similar observation has also been discussed in Co$_2$TiX$_n$. The plot of Berry curvature shows that there is significant mixing of trivial surface states with Fermi arc states as well. The topological character of the Weyl semimetals can be indirectly confirmed by the presence of AHC as discussed below, Anomalous Nernst effect, difference in the scattering process among topologically protected Fermi arc surface states to the trivial states, etc.

### 3.5. AHC of Co$_2$MnGe

Heusler materials exhibiting Weyl points typically show large AHC. The value of AHC depends on the proximity of Weyl points to the Fermi level and the separation between Weyl nodes of opposite chirality in momentum space. A range of AHC values have been reported for Heusler materials: Co$_2$TiSn shows AHC of $\approx 100 \Omega^{-1} \text{cm}^{-1}$ while Co$_2$MnAl shows high AHC of $\approx 2000 \Omega^{-1} \text{cm}^{-1}$.[47] The intrinsic AHC conductivity $\sigma_{xy}$ is calculated using

$$\sigma_{xy} = -\frac{e^2}{h} \int_{BZ} \frac{d^3k}{(2\pi)^3} f_n(k) \Omega^\alpha(k)$$

where $\Omega^\alpha(k)$ is the Berry curvature computed using Equation (1) and $f_n(k)$ is the Fermi–Dirac distribution function. The plot of AHC overlayed on top of the spin-resolved density of states for Co$_2$MnGe is shown in Figure 8. We predict AHC of $140 \Omega^{-1} \text{cm}^{-1}$, which falls in between the AHC calculated for Co$_2$MnSi ($228 \Omega^{-1} \text{cm}^{-1}$) and Co$_2$MnSn ($118 \Omega^{-1} \text{cm}^{-1}$).[47] Given the similarities in the electronic structure of the Co$_2$MnX compounds and the SOC effect on the band crossings having major contributions from Co and Mn orbitals, a difference in AHC for these three compounds is expected to depend on the relative energy position of the node-line crossing. For instance, from the AHC plot we see a large AHC $0.6 \text{eV}$ below the Fermi energy in Co$_2$MnGe; on the other hand, for Co$_2$MnAl the closeness of the crossing to the Fermi energy dictates its much higher AHC.[44] The density of states in Figure 8 and band structures in Figure 1 show that these Co-based Heusler compounds exhibit half-metallic character, and we expect full spin polarization of charge Hall currents.[48,49]
4. Conclusion

We studied a family of Co-based Heusler compounds Co₂MnX (X = Si, Ge, or Sn) as magnetic topological Weyl semimetals. These materials are ferromagnetic with a magnetic moment $M = 5 \mu_B$ per formula unit. Through spin-resolved band structure, we show that these materials exhibit two topologically interesting band crossings in the majority spin channel near the Fermi level. Using Co₂MnGe as an example, we discuss the nodal-line features corresponding to the two band crossings near the Fermi level. Several nodal lines are shown to be present in the system which are protected by different mirror-symmetry planes. These nodal lines show complex 3D features, some of which are entangled. In the presence of spin–orbit coupling and finite magnetization in the system, mirror symmetry is preserved only in the plane perpendicular to the magnetization direction and is broken along other mirror planes. Consequently, the nodal lines are gapped and Weyl points emerge along those broken symmetry planes. We show the presence of Weyl nodes of opposite chiralities in Co₂MnGe, which are the source and sink of Berry curvature. We also predict AHC of $228 \Omega^{-1} \text{cm}^{-1}$ for Co₂MnGe, and $118 \Omega^{-1} \text{cm}^{-1}$ for Co₂MnSn.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

anomalous Hall conductivity, Heusler, nodal lines, Weyl nodes, Weyl semimetals

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Figure 8. AHC ($\sigma^s$) and spin-resolved density of states for Co₂MnGe.
[22] J. A. Logan, S. J. Patel, S. D. Harrington, C. M. Polley, B. D. Schultz, T. Balasubramanian, A. Janotti, A. Mikkelsen, C. J. Palmstrøm, Nat. Commun. 2016, 7, 11993.

[23] G. Chang, S.-Y. Xu, H. Zheng, B. Singh, C.-H. Hsu, G. Bian, N. Alidoust, I. Belopolski, D. S. Sanchez, S. Zhang, H. Lin, M. Z. Hasan, Sci. Rep. 2016, 6, 38839.

[24] G. Chang, S.-Y. Xu, X. Zhou, S.-M. Huang, B. Singh, B. Wang, I. Belopolski, J. Yin, S. Zhang, A. Bansil, H. Lin, M. Z. Hasan, Phys. Rev. Lett. 2017, 119, 156401.

[25] P. van Engen, K. Buschow, M. Erman, J. Magnet. Magnet. Mater. 1983, 30, 374.

[26] P. Webster, J. Phys. Chem. Solids 1971, 32, 1221.

[27] P. Hohenberg, W. Kohn, Phys. Rev. 1964, 136, B864.

[28] W. Kohn, L. J. Sham, Phys. Rev. 1965, 140, A1133.

[29] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, K. Burke, Phys. Rev. Lett. 2008, 100, 136406.

[30] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.

[31] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.

[32] P. E. Blochl, Phys. Rev. B 1994, 50, 17953.

[33] G. Kresse, D. Joubert, Phys. Rev. B 1999, 59, 1758.

[34] A. A. Mosto, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, N. Marzari, Comput. Phys. Commun. 2014, 185, 2309.

[35] Q. Wu, S. Zhang, H.-F. Song, M. Troyer, A. A. Soluyanov, Comput. Phys. Commun. 2018, 224, 405.

[36] S. F. Cheng, B. Nadgomy, K. Bussmann, E. E. Carpenter, B. N. Das, G. Trotter, M. P. Raphael, V. G. Harris, IEEE Trans. Magn. 2001, 37, 2176.

[37] A. Sztyla, A. Kolodziejczyk, H. Rzany, J. Todorović, A. Wanic, Phys. Status Solidi (A) 1972, 11, 57.

[38] G. H. Fecher, H. C. Kandpal, S. Wurmehl, C. Felser, G. Schonhense, J. Appl. Phys. 2006, 99, 08J106.

[39] I. Galanakis, P. H. Dederichs, N. Papanikolaou, Phys. Rev. B 2002, 66, 174429.

[40] H. C. Kandpal, G. H. Fecher, C. Felser, J. Phys. D: Appl. Phys. 2007, 40, 1507.

[41] S. Andrieu, A. Neggache, T. Hauet, T. Devolder, A. Hallal, M. Chshiev, A. M. Bataille, P. Le Fevre, F. Bertran, Phys. Rev. B 2016, 93, 094417.

[42] S. Piccozzi, A. Continenza, A. J. Freeman, Phys. Rev. B 2002, 66, 094421.

[43] T. Kono, M. Kakoki, T. Yoshikawa, X. Wang, K. Goto, T. Muro, R. Y. Umetsu, A. Kimura, Phys. Rev. Lett. 2020, 125, 216403.

[44] P. Li, J. Koo, W. Ning, J. Li, L. Miao, L. Min, Y. Zhu, Y. Wang, N. Alem, C.-X. Liu, Z. Mao, B. Yan, Nat. Commun. 2020, 11, 3476.

[45] A. Sakai, Y. P. Mizuta, A. A. Nugroho, R. Sihombing, T. Koretsune, M.-T. Suzuki, N. Takemori, R. Ishii, D. Nishio-Hamane, R. Arita, P. Goswami, S. Nakatsuji, Nat. Phys. 2018, 14, 1119.

[46] R. Batabyal, N. Morali, N. Avraham, Y. Sun, M. Schmidt, C. Felser, A. Stern, B. Yan, H. Beidenkopf, Sci. Adv. 2016, 2, 1600709.

[47] A. Kubler, C. Felser, Phys. Rev. B 2012, 85, 012405.

[48] J.-C. Tung, G.-Y. Guo, New J. Phys. 2013, 15, 033014.

[49] H.-L. Huang, J.-C. Tung, G.-Y. Guo, Phys. Rev. B 2015, 91, 134409.