Stability of Weyl points in magnetic half-metallic Heusler compounds

Stanislav Chadov, Shu-Chun Wu, and Claudia Felser
Max-Planck-Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

Iosif Galanakis
Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece

(Dated: February 16, 2017)

We employ ab-initio fully-relativistic electronic structure calculations to study the stability of the Weyl points in the momentum space within the class of the half-metallic ferromagnetic full Heusler materials, by focusing on Co₂TiAl as a well-established prototype compound. Here we show that both the number of the Weyl points together with their \( k \)-space coordinates can be controlled by the orientation of the magnetization. This alternative degree of freedom, which is absent in other topological materials (e.g. in Weyl semimetals), introduces novel functionalities, specific for the class of half-metallic ferromagnets. Of special interest are Weyl points which are preserved irrespectively of any arbitrary rotation of the magnetization axis.

PACS numbers: 75.30.-m, 75.10.Lp, 75.50.-y, 75.70.Tj

The transfer of concepts between different disciplines and fields of science has triggered the appearance and growth of new research fields. One of the most striking recent examples is the notion of topology in condensed matter physics and materials science. Following the discovery of topological insulators (see Refs. \[1\] and \[2\] and references therein), it was suggested theoretically that the band structures of Na₃Bi and Cd₃As₂ show Dirac-like energy cones at the Fermi surface \[3, 4\]. Theoretical predictions were confirmed in 2014 and the compounds where named as Dirac Semimetals \[5\]. These findings initiated even more intense interest on the topological effects and the role of the breaking of symmetries was investigated \[6\].

In condensed matter physics the spin degeneracy at a general \( k \)-point is protected by the coexistence of time-reversal symmetry and inversion symmetry, the so-called Kramer degeneracy. Breaking only one of the two symmetries breaks a Dirac point into two Weyl points (WPs) of opposite chirality. Thus there are two types of Weyl semimetals: (a) magnetic Weyl semimetals where inversion symmetry is kept and (b) nonmagnetic noncentrosymmetric ones where time-reversal symmetry is kept (for an extensive review on Weyl semimetals see Ref. \[7\]). Two types of WP’s can occur: type-I, which are isolated points in the Brillouin zone and type II representing a closed loop. There are also rare cases of semimetals, like SrSi₂, where both the inversion and time-reversal are broken leading to the formation of an exotic double Weyl fermion \[8\].

The search for WPs in magnetic systems is a nontrivial task. First, experimentally ARPES measurements of the magnetic Weyl materials are very difficult due to the complex domain structure and thus there is still no material definitely confirmed to be a magnetic Weyl semimetal \[7\]. Second, theoretically the search for WPs in the 3D reciprocal space is rather complicated, since the WPs might be general points of the Brillouin zone and not just along high symmetry axes. Similar manifolds might be formed also by normal degeneracies along the high symmetric directions. In the case of the magnetic systems such symmetry analysis requires the Shubnikov type-II groups and becomes even more complicated.

Among the Heusler compounds \[9, 10\], the ones being half-metallic ferromagnets have attracted considerable attention due their potential applications in spintronics \[11, 12\]. Their most striking characteristic is the so-called Slater-Pauling behavior of the total spin magnetic spin moment which scales linearly with the number of valence electrons \[13, 14\]. This large family provides flexible possibilities to tune their electronic structure, e.g. by shifting the Fermi energy with chemical composition. Due to the very large number of Heusler compounds, it is natural to search for WPs either in the nonmagnetic semi-Heuslers which crystalize in a non-centrosymmetric lattice \[15\], or among the regular magnetic ones crystallizing in the L2₁ structure (space group Fm\(\bar{3}\)m (225)). Their cubic crystalline structure results into a low magneto-crystalline anisotropy, thus their magnetization can be easily manipulated using an external magnetic field, both in single-crystalline as well as polycrystalline samples. Since the L2₁ structure is centrosymmetric, the appearance of magnetism breaks the time-reversal symmetry leading possibly to the appearance of WPs.

Within 2016 three articles have appeared focusing on the WPs in magnetic Heusler compounds. Kübler and Felser suggested that in the case of Co₂MnAl the appearance of a large anomalous Hall effect is linked to four WPs just above the Fermi level \[16\]. Wang and collaborators studied several Co-based Heusler compounds focusing especially on Co₂ZrSn and found that when the magnetization is along the [110] direction there are at least two WPs close to the Fermi level separated by a large distance in the reciprocal space giving rise to well-
FIG. 1: Calculated electronic band structure of Co$_2$TiAl using the scalar-relativistic formalism. The zero energy in the vertical axis is the Fermi level. We have denoted the six crossing points of interest with the symbols: A, B, C, D, E and F. Note that all high symmetry-points are within the $k_z = 0$ plane.

defined Fermi arcs [17]. Finally Chang and collaborators studied the Co$_2$Ti(Si, Ge or Sn) compounds and found another two WPs in the $K - \Gamma$ direction which are different than the ones mentioned just above [18]. Ab-initio calculations in both Refs. [17] and [18] revealed that the different magnetization axis cannot be energetically distinguished probably due to the very high symmetry of the lattice. Thus the important question rises concerning the stability of the observed WPs with respect to the magnetization axis which can be rotated due to external magnetic fields. The answer to this question is primordial for applications since in most cases polycrystalline films are used and thus an external magnetic field would oblige the different domains to have their magnetization along different crystallographic axis and thus the number of interesting band crossings might be substantially reduced. The most interesting band crossings would be those which survive upon arbitrary rotation of the magnetization.

To study them, we consider a typical representative of the Co$_2$-based Heusler family, namely Co$_2$TiAl, which has been well established experimentally and theoretically as a good half-metallic ferromagnet obeying the Slater-Pauling rule; it has 25 valence electrons per formula unit with a total spin magnetic moment of 1 $\mu_B$ per formula unit [13]. We have also studied Co$_2$TiSi and Co$_2$VAl which have 26 valence electrons, and results and conclusions were also similar for them with the only noticeable difference being that the WPs were lower in energy due to the extra electron as expected; the Fermi level in Heuslers can be varied within a rather wide range by changing the chemical composition [12]. In all cases we have used the experimental lattice constants [19, 20]. To perform the electronic structure calculations, we employed the full-potential nonorthogonal local-orbital minimum-basis band structure scheme (FPLO) [21] within the generalized gradient approximation (GGA) [22]. We performed first scalar-relativistic and then fully-relativistic calculations where the Dirac-like analogue to Kohn-Sham equations are solved [21].
FIG. 2: Orbital character of the bands which cross at the six points along the \( K - \Gamma - W \) direction shown in Fig. 1.

As the quantization axis we have considered three cases: [001], [110] and [111]. During the self-consistency, for the Brillouine zone integration a Monkhorst-Pack \( 30 \times 30 \times 30 \) grid has been used \cite{23}. Total energies have been converged with an accuracy of \( 10^{-8} \) in Hartree. Band structure plots have been plotted within the \( k_z = 0 \) plane for all cases considering a very dense division of 500 \( \mathbf{k} \)-points between two consecutive high symmetry points.

We will start our discussion from the scalar-relativistic band structure obtained for \( \text{Co}_2\text{TiAl} \) and presented in Fig. 1. In this case we can decompose the bands in pure majority- and minority-spin character. The minority-spin band structure presents a direct gap at the \( \Gamma \) point of about 0.5 eV typical for half-metallic Heusler compounds and the total spin magnetic moment of 1 \( \mu_B \) in agreement with the Slater-Pauling rule \cite{13}. All high-symmetry points in Fig. 1 have been chosen within the \( k_z = 0 \) plane perpendicular to the \( z \)-axis; \( \Gamma, X, W \) and \( K \) coordinates in the reciprocal space are \( [0 0 0], [1 0 0], [1 1 2 0] \) and \( [3 4 3 0] \), respectively, in \( \frac{2\pi}{a} \) units where \( a \) is the lattice constant. Due to the existence of three transition metal atoms per formula unit, there is a very large number of \( d \) bands around the Fermi level in a narrow energy region (for the character of the bands see Ref. \cite{13}). As a result several crossings which can be considered as potential WPs occur not only along the high symmetry lines shown in Fig. 1 but in the whole Brillouin zone.

In order to make our study possible we have focused on six crossing points along the \( K - \Gamma \) direction which have their exact symmetry analog in the \( \Gamma - W \) direction as shown in Fig. 1. The \( \Gamma - K \) direction has been proposed to contain the WPs according to Refs. \cite{17} and \cite{18}. The energy window under study which contains the relevant WPs is between the Fermi level and 2 eV above it \( (0 < E - E_F < 2 \text{ eV}) \) as shown in Fig. 1. A detailed analysis of the band structure using the so-called fat band scheme \cite{24} revealed the character of the bands which cross and we present in Fig. 2 the bands orbital character as deduced using the fat band scheme. The minority-spin band at the A and B points, which have been proposed to be WPs in Ref. \cite{18}, belongs to the double degenerate \( e_u \) bands which have exclusively their weight at the Co atoms (see Ref. \cite{13} for an extended discussion of the character of the bands). This band at the point B crosses a majority-spin band made up of states belonging the triple-degenerate antibonding \( t_{2g} \)
As a first step using the fully-relativistic formalism we have computed the band structure choosing as quantization-axis the [100] and [001] simulating this way the effect of the external magnetic field on the direction of the magnetization, and we present our results in Fig. 3 focusing above the Fermi level and in the $K - \Gamma - W$ direction. To facilitate the discussion we have encircled with red color the cases where the degeneracy is lost and there is no crossing anymore and with green when the crossing is preserved. In the Dirac relativistic formalism spin is no more a good quantum number and thus we cannot project our band structures on spin. When the quantization axis is along the [100] direction then only the $M_x$ mirror plane which is normal to the [100] direction and the fourfold $C_{4z}$ rotational axis survive. As a result in the $k_z = 0$ plane only the WP at points B is preserved. The $k_y = 0$ is equivalent to $k_z = 0$ plane and the question is what happens in the $k_z = 0$ plane normal to the [100] axis. To answer this question we have considered as quantization axis the [001] and now the $k_z = 0$ plane in the lower panel of Fig. 3 corresponds to the $k_x = 0$ plane in the case of the [100] axis. We can see that now at the points D and F the degeneracy is preserved. Thus in magnetic materials the situation is much more complicated than the one expected for magnetic semimetals [7]. We have performed fully-relativistic calculations also considering the [110], [011] and [111] as the quantization axis. Now the symmetry operations are different in each case, e.g. in the [110] case the symmetry operations -except the inversion symmetry- which are preserved are the mirror plane $M_{xy}$ which is normal to the [110] axis and the $C_{[110]}^2$ rotation. Presented band structures suggest that different crossing points are conserved in each case.

To further analyze the behavior of the crossing points we focused on the ones marked as A, B, C and D in Fig. 1 since F is equivalent to D and E to C. In this case there are 12 equivalent $I$-$K$ directions allowed by the Fm$ar{3}$m space-group. In order to distinguish between spin states in the fully-relativistic regime, we have employed the Korringa-Kohn-Rostoker (KKR) electronic structure method employing relativistic spin-projection operators [25]. For the usual spin-polarized case without the spin-orbit coupling KKR yields a similar band structure to the FPLO one, presented in Fig. 1. In order to track the appropriate changes induced by the spin-orbit coupling with respect to the simply spin-polarized ones, we will simultaneously depict all 12 points of each type (A, B, C and D) on the same $\Gamma$-centered sphere in the 3D $k$-space, by tuning its radius precisely to host the given point type (and simultaneously tuning the corresponding energy). Such representation allows to compare their character together with its evaluation by changing the magnetization orientation (see Fig. 4).

In Fig. 4 we consider three distinct orientations of the magnetization: $\vec{M} \parallel [001]$, [111] and [110]. We also decompose the spectral density into the majority- and minority-spin (using red and blue colors for the spectral
density, respectively). By considering, for example, the sphere containing the point A (A-sphere), we see that it has an anticrossing character for all \( k \)-directions and magnetization orientations except for \( \vec{M} \parallel [110] \), where it keeps crossing along \( \vec{k} \parallel [110] \) (and along the equivalent \([1\overline{1}0]\) which is just hidden behind). One partially observes this also in the corresponding \( E(k) \) plots (shown only for two nonequivalent directions): encircling of the A-points is shown in red everywhere (anticrossing) except of \( \vec{k} \parallel [110] \) for \( \vec{M} \parallel [110] \) case (green). This means that by taking the polycrystalline case, the overall contribution of the A-crossing into the transport properties (provided it is tuned to the Fermi energy) will be drastically reduced. The same situation occurs for the C-type, which keeps crossing only along \( \vec{k} \parallel [110] \) (and \([1\overline{1}0]\)) for \( \vec{M} \parallel [110] \) case. The intermediate situation occurs for the D-type which has a pure minority-spin character: for \( \vec{M} \parallel [001] \) it gives crossing characters in four xy-directions: \([1\overline{1}0], [\overline{1}10], [1\overline{1}0] \) and \([\overline{1}10]\), six crossings in case of \( \vec{M} \parallel [111] \), and six - in case of \( \vec{M} \parallel [110] \). In contrast to A, C, and D, the B-point exhibits the most universal behavior: it preserves the crossing character in all \( k \)-directions for all magnetization orientations. This indicates, that by tuning the Fermi energy to the B-point, its efficient overall transport response might be achieved even in the polycrystalline case.

Employing ab-initio calculations within the fully-relativistic Dirac-formalism we studied the stability of Weyl points in magnetic half-metallic Heusler compounds using Co\(_2\)TiAl as a prototype. Our results suggest that the preservation of the crossing points observed in the scalar-relativistic band structure strongly depends on the orientation of the quantization axis due to the broken symmetry operations. Moreover due to symmetry reasons the band structure within the \( k_x = 0 \), \( k_y = 0 \) and \( k_z = 0 \) plane differs for a given quantization axis making the identification of the Weyl points which are preserved even more complex. In the case of Co\(_2\)TiAl we found that there is a crossing which is invariant to the rotation of the magnetization axis and thus it is a real Weyl point.

Our results clearly show that external magnetic fields, which pin the quantization axis in magnetic half-metals, affect the number and the momentum space location of Weyl points offering novel possibilities, not present in conventional Weyl semimetals, in the field of topological materials.

Authors acknowledge fruitful discussion with G. H. Fecher. One of the authors (IG) gratefully acknowledges the financial support by the Max-Planck Gesellschaft.

* Electronic address: stanslav.chadov@cpfs.mpg.de
† Electronic address: galanakis@upatras.gr

[1] Y. Ando, Topological Insulator Materials, J. Phys. Soc. Jpn. 82, 102001 (2013).
[2] A. Bansil, H. Lin, and T. Das, Colloquium: Topological band theory, Rev. Mod. Phys. 88, 021004 (2016).
[3] Z. J. Wang, Y. Sun, X. Q. Chen, C. Franchini, G. Xu, H. M. Weng, X. Dai, and Z. Fang, Dirac semimetal and topological phase transitions in A\(_3\)Bi (A = Na, K, Rb), Phys. Rev. B 85, 195320 (2012).
[4] Z. J. Wang, H. M. Weng, Q. S. Wu, X. Dai, and Z. Fang, Three dimensional Dirac semimetal and quantum transport in Cd\(_3\)As\(_2\), Phys. Rev. B 88, 125427 (2013).
[5] Z. Liu et al., Discovery of a three-dimensional topological Dirac semimetal, Na\(_3\)Bi, Science 343, 864 (2014).
[6] B. Bradlyn, J. Cano, Z. Wang, M. G. Vergniory, C. Felser, R. J. Cava, and B. A. Bernevig, Beyond Dirac and Weyl fermions: Unconventional quasiparticles in conventional crystals, unpublished, preprint: arXiv:1603.03093.
[7] H. Weng, Xi Dai, and Z. Fang, Topological semimetals predicted from first-principles calculations, J. Phys.: Condens. Matter 28, 303001 (2016).
[8] S.-M. Huang et al., New type of Weyl semimetal with quadratic double Weyl fermions, PNAS 113, 1180 (2016).
[9] F. Heusler, Kristallstruktur und Ferromagnetismus der Mangan-Aluminium-Kupferlegierungen, Verh. Dtsch. Phys. Ges. 12, 219 (1903).
[10] F. Heusler and E. Take, The nature of the Heuslers alloys, Phys. Z. 13, 897 (1912).
[11] A. Hirohata and K. Takenashi, Perspectives of Heusler compounds, J. Phys. D: Appl. Phys. 47, 195001 (2014).
[12] "Heusler Alloys. Properties, Growth,, Applications", C. Felser and A. Hirohata (Eds.), Springer Series in Materials Science Vol. 222, Springer International Publishing (2016).
[13] I Galanakis, P. H. Dederichs, and N. Papanikolaou, Slater-Pauling behavior and origin of the half-metallicity of the full-Heusler alloys, Phys. Rev. B 66, 174429 (2002).
[14] T. Graf, C. Felser, and S. S. P. Parkin , Simple rules for the understanding of Heusler compounds, Progress in Solid State Chemistry 39, 1 (2011).
[15] S.-Y. Lin, M. Chen, X.-B. Yang, Y.-J. Zhao, S.-C. Wu, C. Felser, and B. Yan, Theoretical search for half-Heusler topological insulators, Phys. Rev. B 91, 094107 (2015).
[16] J. Küberl and C. Felser, Weyl points in the ferrimagnetic Heusler compound Co\(_3\)MnAl, EPL 114, 47005 (2016).
[17] Z. Wang, M. G. Vergniory, S. Kushwaha, M. Hirschberger, E. V. Chulkov, A. Ernst, N. P. Ong, R. J. Cava, and B. A. Bernevig, Time-Reversal Breaking Weyl Fermions In Magnetic Heuslers, Phys. Rev. Lett. 117, 236401 (2016).
[18] G. Chang, S.-Y. Xu, H. Zheng, B. Singh, C.-H. Hsu, G. Bian, N. Alidoust, I. Belopolski, D. S. Sanchez, H. Lin, and M. Z. Hasan, Room-temperature magnetic topological Weyl fermion and nodal semimetal states in half-metallic Heusler Co\(_2\)TiX (X=Si, Ge, or Sn), Scientific Report 6, 38839 (2016).
[19] K. H. J. Buschow, P.G. van Engen, and R. Jongebruer, Magneto-optical properties of metallic ferromagnetic materials, J. Magn. Magn. Mat. 38, 1 (1983).
[20] J. Barth, G. H. Fecher, B. Balke, T. Graf, C. Felser, A. Shkabko, and A. Weidenkaff, Anomalous transport properties of the halfmetallic ferromagnets Co\(_2\)TiSi, Co\(_2\)TiGe, and Co\(_2\)TiSn, Phil. Trans. R. Soc. A 369, 3588 (2011).
[21] K. Koepernik and H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis band-structure scheme,
Phys. Rev. B 59, 1743 (1999).

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

[23] H. J. Monkhorst and J. D. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13, 5188 (1976).

[24] I. Galanakis, K. Özdoğan, and E. Şaşoğlu, Half-metallic antiferromagnetism in Cr$_{2+x}$Se ($0 \leq x \leq 1$): A first-principles study, Phys. Rev. B 86, 134427 (2012).

[25] H. Ebert, D. Koedderitzsch, and J. Minar, Calculating condensed matter properties using the KKR-Green’s function method: recent developments and applications, Rep. Prog. Phys. 74, 096501 (2011).