Topological electronic structure and Weyl points in nonsymmorphic hexagonal materials

Rafael González-Hernández,†, 1, 2 Erick Tuiran,1, † and Bernardo Uribe‡

1 Departamento de Física y Geociencias, Universidad del Norte, Km. 5 Vía Antigua Puerto Colombia, Barranquilla 080020, Colombia
2 Institut für Physik, Johannes Gutenberg Universität Mainz, D-55099 Mainz, Germany
3 Departamento de Matemáticas y Estadística, Universidad del Norte, Km. 5 Vía Antigua Puerto Colombia, Barranquilla 080020, Colombia

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Using topological band theory analysis we show that the nonsymmorphic symmetry operations in hexagonal lattices enforce Weyl points at the screw-invariant high-symmetry lines of the band structure. The corepresentation theory and connectivity group theory show that Weyl points are generated by band crossings in accordion-like and hourglass-like dispersion relations. These Weyl points are stable against weak perturbations and are protected by the screw rotation symmetry. Based on first-principles calculations we found a complete agreement between the topological predicted energy dispersion relations and real hexagonal materials. Topological charge (chirality) and Berry curvature calculations show the simultaneous formation of Weyl points and nodal-lines in $4d$ transition-metal trifluorides such as AgF$_3$ and AuF$_3$. Furthermore, a large intrinsic spin-Hall conductivity was found due to the combined strong spin-orbit coupling and multiple Weyl-point crossings in the electronic structure. These materials could be used to the spin/charge conversion in more energy-efficient spintronic devices.

INTRODUCTION

The intersection between band-theory of solids and topology has recently attracted a lot of interest in the condensed matter physics community. In the past decade, topological insulators opened the door to novel phases of matter with unique properties [1]. The field of topological phases has rapidly expanded and new kind of topological phases have appeared, including Chern insulators [2], topological insulators [3], crystalline topological insulators [4], Dirac semimetals [5], Weyl semimetals [6] and nodal-line semimetals [7] among others. Weyl semimetals have been the subject of intensive research because they were the first topological material found without a bulk energy gap which is protected by the nontrivial topology of the band structure [6]. The existence of Weyl semimetals was predicted theoretically about ten years ago and was finally found experimentally in 2015 [8].

It is theoretically known that a Weyl semimetal can only arise in a crystal where time-reversal symmetry or inversion symmetry is broken [9]. For these cases the Hamiltonian around the Weyl point can be written as a 2×2 Weyl equation, where the energy crossings are linearly dispersing energy-bands which act as monopoles of Berry curvature in momentum space [8]. These monopole charges are characterised by quantised topological charge (or chirality) and in the exclusive presence of Weyl points the net chiral charge is zero (this result is known as the Nielsen-Ninomiya theorem [10]). However, the space group symmetries in solids can be complicated and high-order Weyl crossings [11, 12] or Weyl points and nodal-lines combinations can be present at the material.

The variety of topological band crossing in materials is the essential ingredient that guarantees the existence of the novel charge and spin transport properties that Weyl semimetals show [13]. Therefore, the generation of new materials with stable Weyl points is an emergent field of great interest from a fundamental point of view and possible technological applications. Generally, Weyl points in the band structure can be emergent by the nonsymmorphic symmetries of the crystal, like screw and glide crystal symmetries; they are commonly called symmetry-enforced energy band crossings. Previous works have investigated several nonsymmorphic energy band crossings [14, 15] and the possible materials realisation [16, 17]. In particular, Weyl points protected by screw rotations and Weyl nodal lines protected by glide reflections were reported recently in trigonal and hexagonal lattices [18, 19].

In this work, we study the generation of Weyl points due to the screw nonsymmorphic symmetry in hexagonal systems with the P6$_3$ and P6$_p$22 space groups. First, based on corepresentation theory [20] and band connectivity group theory, we predict the combinatorics of the complete electronic band structure. We note the appearance of accordion-like and hourglass-like energy dispersion relations inducing the existence of Weyl points protected by the screw and time-reversal symmetries. Second, using first-principles calculations we corroborate the energy band crossings for hexagonal materials. In particular we analyse the electronic band structure of the materials In$_2$Se$_3$, KCaNd(PO$_4$)$_2$, P$_3$, AgF$_3$, AuF$_3$, TaGe$_2$ and Nb$_3$CoS$_6$. Third, we focus our analysis on the topological properties of the Weyl points in AgF$_3$ and AuF$_3$ materials. These are possible Weyl-semimetal candidates with inversion symmetry breaking. Following the double
femion theorem, we predict the presence of both Weyl points and nodal lines at AgF$_3$ and AuF$_3$. We find interesting distributions of Weyl points as it is the case of the second and third conduction bands of AgF$_3$ where we find 6 Weyl points with +2 chirality, 24 points with +1 chirality and 36 points with −1 chirality. This analysis of the distribution of Weyl points allows us to confirm that the Weyl points do not necessarily come in pairs with opposite chirality [12]. Finally, we analyse the spin transport properties and we find a strong spin-Hall effect due to the presence of Weyl fermions in the valence band of AgF$_3$ and AuF$_3$ materials. This interesting spin-transport property in 4d transition-metal fluorides may help in the quest for the use of Weyl nodes in developing the next-generation of energy-efficient information technology [21].

**REPRESENTATION THEORY**

**Symmetries**

Let us start by recalling the hexagonal materials with screw rotation symmetries. For this consider the symmetries:

\[ Q_{6,p} : (x, y, z) \mapsto (y, -x + y, z + \frac{a}{6}) \]
\[ Q_{π,p} : (x, y, z) \mapsto (-x, y, z) \]
\[ C_3 : (x, y, z) \mapsto (-x + y, -y, z) \]
\[ M_r : (x, y, z) \mapsto (y, x, -z + 2r) \]

Together with the translational symmetries of the axis $T_x, T_y, T_z$ whenever the canonical vectors on the $x$ and the $y$ axes define an hexagonal lattice.

The groups of interest of this work are the ones that are generated by the translational symmetries and combinations of the above-defined symmetries. The space groups, the generators, and the relations are summarised the following list (commuting relations are not listed):

\[ P6_1(#169) : Q_{6,1} \]
\[ P6_5(#170) : Q_{6,1} \]
\[ P6_2(#171) : Q_{6,4}, C_2 \]
\[ P6_4(#172) : Q_{6,2}, C_2 \]
\[ P6_3(#173) : Q_{6,3}, C_3 \]
\[ P6_322(#178) : Q_{6,1}, M_{1,\hat{z}}, M_{3,\hat{z}}, Q_{6,1}, M_{1,\hat{x}} = Q_{6,1}^{-1} \]
\[ P6_322(#179) : Q_{6,1}, M_{1,\hat{x}}, M_{3,\hat{x}}, Q_{6,1}, M_{1,\hat{z}} = Q_{6,1}^{-1} \]
\[ P6_322(#180) : Q_{6,4}, C_2, M_{1,\hat{y}}, M_{3,\hat{y}}, Q_{6,4}, M_{1,\hat{z}} = Q_{6,4}^{-1} \]
\[ P6_322(#181) : Q_{6,2}, C_2, M_{4,\hat{y}}, M_{2,\hat{y}}, Q_{6,2}, M_{4,\hat{x}} = Q_{6,2}^{-1} \]
\[ P6_322(#182) : Q_{6,3}, C_3, M_0, M_0, Q_{6,3}, M_0 = Q_{6,3}^{-1} \]
\[ M_0 C_3 M_0 = C_3^{-1} \]

The induced action on the momentum space $(k_x, k_y, k_z)$ of all the symmetries $Q_{6,p}$ is simply a six-fold rotation, and the induced action of all the $M_r$'s simply interchanges $k_z$ with $k_y$ and sends $k_x$ to $-k_z$. The time-reversal operator will be denoted $\mathbb{T}$ and it acts on the momentum coordinates as $\mathbb{T}(k_x, k_y, k_z) = (-k_x, -k_y, -k_z)$.

The time-reversal operator acts on electronic states with the property that $\mathbb{T}^2 = 1$ whenever there is no spin-orbit coupling (NOSOC) or spinless particles, and $\mathbb{T}^2 = -1$ whenever there is spin-orbit coupling (SOC) interaction or half-integer spin particles.

The information of the Brillouin zone in momentum space for all these groups appears encoded in Figure 1. Here we have borrowed the notation from the Bilbao Crystallographic Server [22] [24].

Each cell (high-symmetry points, lines and planes) in the Brillouin zone is fixed by certain operators, and the group that these operators define is called the isotropy group of the cell. Some of the topological information of the crystal may be deduced by restricting the attention to the operators $Q$ and $M$. Note that the induced actions of the rotations $C_2$ and $C_3$ on the Brillouin zone are the same as the actions of $Q^3$ and $Q^2$ respectively. In the table that appears in Table 1 we list the subgroups of the isotropy groups generated by these elements localised in specific cells of the Brillouin zone (see Figure 1).

Note that on the 1-cells (high-symmetry lines) $Γ-A$ and $L-M$ the isotropy groups of the boundary 0-cells (high-symmetry points) are bigger than the ones of the interior of the 1-cell. Also, note that the time-reversal operator fixes the boundary 0-cells and not the interior. This information, together with the fact that the operator $Q$ rotates and translates, induces a very interesting topological structure on the energy bands on these paths. In [25] the energy bands for the symmetry groups $P6_6$ were studied on the paths $Γ-A$ and $L-M$. Here we will extend the study to the groups $P6_622$ and we will furthermore

![Brillouin zone for the hexagonal Bravais lattice](http://www.cryst.bilbao.es)
analyse the band structures for the path K-H and on the horizontal paths. To carry out this analysis we need to recall some results in the classification of corepresentations.

Corepresentations

A corepresentation is the name that Wigner [20, §26] assigned when there is a complex representation of a group on which half of its elements act as unitary operators and the other half as antiunitary operators. Since the time-reversal operator is antiunitary, the isotropy groups of the cells may include antiunitary operators and therefore their representations are corepresentations.

Denote the isotropy group \( G \) and let \( G_0 \) be its subgroup of unitary operators. A corepresentation of \( G \) restricts to a complex representation of the group \( G_0 \) and the classification of the irreducible corepresentations is encoded in the properties of this complex representation. For \( u \in G_0 \) denote by \( \Lambda(u) \) the unitary matrix associated to the chosen representation and denote by \( \Lambda \) the representation of \( G_0 \). Take any antiunitary operator \( a_0 \in G \) and define a conjugate complex representation of \( G_0 \) by the equation

\[
\overline{\Lambda}(u) = \Lambda(a_0^{-1}ua_0)^*.
\]

Now, an irreducible corepresentation of \( G \) can be one of three types. The first type contains only one irreducible representation \( \Lambda \) of the unitary group \( G_0 \) and the second type contains twice the irreducible representation \( \Lambda \oplus \Lambda \); in these two cases \( \Lambda \cong \overline{\Lambda} \). If \( \beta \) is the matrix that transforms \( \Lambda \) into \( \overline{\Lambda} \) then the associated matrix \( M(a_0^2) \) of \( a_0^2 \) satisfies the equation \( \beta \beta^* = \pm M(a_0^2) \). The first type is fulfilled when \( \beta \beta^* = M(a_0^2) \) and the second type when \( \beta \beta^* = -M(a_0^2) \) [20, pp. 343]. The third type is when the complex representations \( \Lambda \) and \( \overline{\Lambda} \) of \( G_0 \) are inequivalent representations and therefore both must appear in the corepresentation.

Antiunitary operators

Note that the previous information only depends on an antiunitary operator with \( \theta^2 = \pm 1 \). Clearly the time-reversal operator is one of such. Nevertheless, when the time-reversal operator (T) does not belong to the isotropy group of the cell it is important to determine the properties of the other antiunitary symmetries which do belong to the isotropy group.

The antiunitary symmetries that we obtain are of the form \( \hat{F}T \) where \( \hat{F} \) is the operator on the Hilbert space which lifts the geometrical action given by \( F \). In momentum space the operators \( F \) and \( T \) commute, but as operators the commuting relation may be affected by a phase factor. Let us first study the case when the geometrical action \( F \) is the composition \( T_aO_R \) of a rotation \( O_R \) by an orthogonal matrix and a translation \( T_a \) by the vector \( a \). Then the operator \( \hat{F} \) equals the composition \( \hat{T}_a\hat{O}_R \).

The operators that lift rotations \( \hat{O}_R \) commute with the time reversal operator

\[
\hat{O}_R T = T \hat{O}_R
\]

because there are no non-trivial complex one dimensional representations of the groups \( SO(3) \) and \( SU(2) \) [20, Eqn. 26.17]. On the other hand the commutation relation of \( \hat{T}_a \) and \( T \) can be deduced by writing the translation operators in terms of Bloch waves. Recall that a Bloch wave is of the form

\[
\psi_k(r) = u_k(r)e^{-ik\cdot r}
\]

where \( u_k(r) \) remains invariant under translation by elements of the lattice of the crystal.

Expanding the composition we obtain:

\[
\hat{T}_a\psi_k(r) = u_k(r+a)e^{-ik\cdot r}e^{-ika}
\]

and in the opposite order we obtain:

\[
\hat{T}_a\psi_k(r) = u_{-k}(r+a)e^{-ik\cdot r}e^{-ika}.
\]

Hence the operators that lift translations commute with the time reversal operator

\[
\hat{T}_a \hat{T} = \hat{T}_a T.
\]
We emphasise here that the vector $a$ does not have to belong to the lattice of symmetries of the crystal for the commutativity to hold. Nevertheless whenever $a$ does belong to the lattice we recover Bloch’s theorem \( \hat{T}_a \psi_k(r) = e^{-ik \cdot a} \psi_k(r) \).

Note that the antiunitary operators $\hat{T}$ and $\hat{M}_r \hat{T}$ both square to 1 on the cells that are fixed by the geometrical operators since either $\hat{T}$, $\hat{M}_r$, and $\hat{T}$ square to 1 whenever there is no SOC, or $\hat{T}$, $\hat{M}_r$, and $\hat{T}$ square to -1 whenever there is SOC interaction.

More interestingly, on the cells which are fixed by the operator $\hat{Q}_{6,p}^{6} T$ we have that

\[
(\hat{Q}_{6,p}^{6} T)^2 |_{k_z=0} = 1
\]

and

\[
(\hat{Q}_{6,p}^{6} T)^2 |_{k_z=\pi} = \begin{cases} 
1 & \text{whenever } p = 2, 4 \\
-1 & \text{whenever } p = 1, 3, 5.
\end{cases} \quad (2)
\]

since by Bloch’s theorem we obtain

\[
(\hat{Q}_{6,p}^{6} T)^2 = \hat{Q}_{6,p}^{6} \hat{Q}_{6,p}^{6} = e^{-ipk_z}.
\]

and we have specialised to the planes $k_z = 0$ and $k_z = \pi$. Here is worth pointing out that the antiunitary operator $\hat{Q}_{6,p}^{6} T$ fixes the points K and H and squares to 1 in K and squares to -1 in H whenever $p$ is odd and squares to 1 whenever $p$ is even. Since the path, K-H is fixed by the group generated by $\hat{Q}_{6,p}^{6}$, we see that Kramer’s degeneracy rule may not occur in all states in K. This fact will be exploited when the topological structure of the bands along the K-H path is analysed.

**TOPOLOGICAL BAND ANALYSIS**

In this section we will analyse the topological structure of the energy bands along all the high-symmetry lines (1-cells). Of particular interest are the vertical 1-cells $\Gamma$-A, M-L, and K-H since the screw rotation operator $\hat{Q}_{6,p}$ endows them with a very interesting form.

We will start with the symmetry groups $P6_p$ and afterwards we will continue with $P6_p22$. We will take only $p = 1, 2, 3$ since the topological structures for $p = 4$ and $p = 5$ are equivalent to the ones of $p = 2$ and $p = 1$ respectively.

For each vertical cell and each $p$ we will also reconstruct the combinatorial band diagrams using the information found in the Bilbao Crystallographic Server (BCS) under the BANDREP menu [26][28]. We will write the compatibility relations of interest, we will construct the associated band representation and we will match this band representation with the one we have constructed. We refer to [26][28] for the explanations on the symbology.

**Symmetry groups $P6_p$**

**Topological band analysis on $\Gamma$-A**

The isotropy groups of the $\Gamma$ and A points are generated by the elements $Q_{6,p}$ and $T$ while the isotropy group of the $\Gamma$-A path is generated only by $Q_{6,p}$. The operators $\hat{Q}_{6,p}$ and $T$ commute and in the presence of SOC interaction they satisfy the equations

\[
\hat{Q}_{6,p}^{6} = e^{-ik \cdot p} \quad \text{and} \quad T^2 = -1.
\]

The operator $\hat{Q}_{6,p}$ may be diagonalised on this path with eigenvalues

\[
\hat{Q}_{6,p}\psi_l(k) = e^{i\pi \frac{p}{3}} e^{-ik \cdot p} \psi_l(k)
\]

with $l \in \{1, 3, 5, 7, 9, 11\}$. Specialising to the points $\Gamma$ and A we obtain the representations

\[
\hat{Q}_{6,p}\psi_l(\Gamma) = e^{i\pi \frac{p}{3}} \psi_l(\Gamma), \quad \hat{Q}_{6,p}\psi_l(A) = e^{i\pi \frac{p}{3}} \psi_l(A).
\]

These representations may be lifted to corepresentations of the groups generated by $\hat{Q}_{6,p}$ and $T$ in the following way. On $\Gamma$ the pairs $\{\psi_l(\Gamma), \psi_{11}(\Gamma)\}$, $\{\psi_3(\Gamma), \psi_9(\Gamma)\}$ and $\{\psi_5(\Gamma), \psi_7(\Gamma)\}$ define irreducible corepresentations of the third type since in this case $\psi_l(\Gamma)$ and $\bar{\psi}_l(\Gamma) = \psi_{12-l}(\Gamma)$ are not isomorphic representations. Therefore on $\Gamma$ the states $\psi_l(\Gamma)$ and $\psi_{12-l}(\Gamma)$ have the same energy.

On A the relation on the representations depends on the value of $p$. For $p = 1$ the pairs $\{\psi_3(A), \psi_{11}(A)\}$ and $\{\psi_5(A), \psi_9(A)\}$ define corepresentations of the third type and both the representations $\psi_1(A)$ and $\psi_{11}(A)$ must appear twice since the operator $T$ forces each of these representations to become quaternionic and therefore they must come in doublets. Hence the corepresentations defined by $\psi_1(A) \oplus \psi_1(A)$ and $\psi_{11}(A) \oplus \psi_{11}(A)$ are of the second type. In this case, the combinatorial description of the band appears in figure [4] where the bands are denoted by the eigenfunctions $\psi_l$ and the values on $\Gamma$ and A are the eigenvalues of the eigenfunctions in $\Gamma$ and A respectively.
Now, from the Bilbao Crystallographic Server (BCS) we obtain the minimal set of compatibility relations:

\[
\Gamma_9 \Gamma_{12}(2) \rightarrow \Sigma_9(1) \oplus \Sigma_{12}(1) \quad 2\Sigma_{12}(2) \leftarrow \Sigma_9 \Sigma_9(2)
\]
\[
\Gamma_7 \Gamma_8(2) \rightarrow \Sigma_7(1) \oplus \Sigma_8(1) \quad 2\Sigma_{11}(2) \leftarrow \Sigma_{10} \Sigma_{10}(2)
\]
\[
\Gamma_{10} \Gamma_{11}(2) \rightarrow \Sigma_{10}(1) \oplus \Sigma_{11}(1) \quad \Sigma_5(1) \oplus \Sigma_{11}(1) \leftarrow \Sigma_8 \Sigma_{12}(2)
\]
\[
\Sigma_8(1) \oplus \Sigma_{10}(1) \leftarrow \Sigma_7 \Sigma_{11}(2).
\]

These representations can be assembled into diagram 5 agreeing completely with diagram 4.

For \( p = 2 \) we have that the pairs \( \{\psi_1(A), \psi_3(A)\} \), \( \{\psi_5(A), \psi_{11}(A)\} \) and \( \{\psi_7(A), \psi_9(A)\} \) define corepresentations of the third type and the combinatorial description of the band appears in diagram 6.

In this case the minimal set of compatibility relations from BCS is:

\[
\Gamma_7 \Gamma_8(2) \rightarrow \Sigma_7(1) \oplus \Sigma_8(1) \quad \Sigma_7(1) \oplus \Sigma_{12}(1) \leftarrow \Sigma_8 \Sigma_9(2)
\]
\[
\Gamma_9 \Gamma_{12}(2) \rightarrow \Sigma_9(1) \oplus \Sigma_{12}(1) \quad \Sigma_9(1) \oplus \Sigma_9(1) \leftarrow \Sigma_{10} \Sigma_{12}(2)
\]
\[
\Gamma_{10} \Gamma_{11}(2) \rightarrow \Sigma_{10}(1) \oplus \Sigma_{11}(1) \quad \Sigma_9(1) \oplus \Sigma_{10}(1) \leftarrow \Sigma_{11} \Sigma_{12}(2),
\]

which leads to the diagram 7 in agreement with diagram 6.

Finally, for \( p = 3 \) the pairs \( \{\psi_1(A), \psi_5(A)\} \) and \( \{\psi_7(A), \psi_{11}(A)\} \) define corepresentations of the third type, and the representations \( \psi_3(A) \) and \( \psi_9(A) \) must appear twice thus making \( \psi_3(A) \oplus \psi_3(A) \) and \( \psi_9(A) \oplus \psi_9(A) \) corepresentations of the second type. The combinatorial structure appears in diagram 8:

The minimal set of compatibility relations from BCS for this case is:

\[
\Gamma_7 \Gamma_8(2) \rightarrow \Sigma_7(1) \oplus \Sigma_8(1) \quad \Sigma_7(1) \oplus \Sigma_{12}(1) \leftarrow \Sigma_7 \Sigma_7(2)
\]
\[
\Gamma_9 \Gamma_{12}(2) \rightarrow \Sigma_9(1) \oplus \Sigma_{12}(1) \quad \Sigma_7(1) \oplus \Sigma_7(1) \leftarrow \Sigma_8 \Sigma_8(2)
\]
\[
\Gamma_{10} \Gamma_{11}(2) \rightarrow \Sigma_{10}(1) \oplus \Sigma_{11}(1) \quad \Sigma_{10}(1) \oplus \Sigma_{12}(1) \leftarrow \Sigma_{11} \Sigma_6(2)
\]
\[
\Sigma_{11}(1) \oplus \Sigma_5(1) \leftarrow \Sigma_{10} \Sigma_{12}(2),
\]

which leads to diagram 9 in agreement with diagram 8.

Parallel to the previous combinatorial description we have carried out computational first-principles calculations of hexagonal materials with the P6_1, P6_2 and P6_3 space groups in order to check the theoretical predicted topological band structures. We have plotted the electronic band structure along the \( \Gamma-A \) path for each space groups in Figure 2 and we can see that the expected combinatorial structures are recovered if we compare them with diagrams 4, 6 and 8. As a by-product of our calculations we notice that a set of Weyl points are generated by the accordion-like (2a) and hourglass-like dispersion figures (2b and c).

**Topological band analysis on M-L**

The isotropy groups of the points M and L are generated by \( Q_{6,p}^3 \) and \( T \) while the isotropy group of the path M-L between the points is only generated by \( Q_{6,p}^3 \). Since \( (Q_{6,p}^3)^2 = -ie^{-i\pi s_p} \) we may diagonalise this operator on the path M-L having eigenvalues

\[
\tilde{Q}_{6,p}^3 \psi_{\pm}(k) = \pm ie^{-i\pi s_p} \psi_{\pm}(k).
\]

Specialising on M and L we obtain the representations

\[
\tilde{Q}_{6,p}^3 \psi_{\pm}(M) = \pm i\psi_{\pm}(M), \quad \tilde{Q}_{6,p}^3 \psi_{\pm}(L) = \pm ie^{-i\pi s_p} \psi_{\pm}(L).
\]
On M the pair \( \{ \psi_+(M), \psi_-(M) \} \) defines a corepresentation of the third type. On L we have that for \( p = 1, 3 \) the representations \( \psi_+(L) \) and \( \psi_-(L) \) must appear twice so that \( \psi_+(L) \oplus \psi_+(L) \) and \( \psi_-(L) \oplus \psi_-(L) \) define representations of the second type. The combinatorial structures from M to L appear in diagram (11) for \( p = 1 \) and in diagram (12) for \( p = 3 \):

\[
\begin{array}{ccc}
M & U & L \\
\vdots & \vdots & \vdots \\
\psi_+ & -i & -1 \\
\psi_- & -i & -1 \\
\end{array}
\]

(11)

\[
\begin{array}{ccc}
M & U & L \\
\vdots & \vdots & \vdots \\
\psi_+ & -i & -1 \\
\psi_- & -i & 1 \\
\end{array}
\]

(12)

The minimal set of compatibility relations from BCS for \( p = 1 \) and \( p = 3 \) is:

\[
\mathcal{M}_3 \mathcal{M}_4(2) \rightarrow \mathcal{U}_3(1) \oplus \mathcal{U}_4(1) \quad 2\mathcal{U}_3(1) \leftrightarrow \mathcal{L}_3 \mathcal{L}_4(2) \\
2\mathcal{U}_4(1) \leftrightarrow \mathcal{L}_4 \mathcal{L}_4(2)
\]

leading to diagram (13). This is in agreement with diagrams (11) and (12):

\[
\begin{array}{ccc}
\mathcal{M}_3 \mathcal{M}_4(2) & \mathcal{U}_4(1) & \mathcal{L}_3 \mathcal{L}_4(2) \\
\mathcal{M}_3 \mathcal{M}_4(2) & \mathcal{U}_4(1) & \mathcal{L}_4 \mathcal{L}_4(2)
\end{array}
\]

(13)

For \( p = 2 \) the pair \( \{ \psi_+(L), \psi_-(L) \} \) defines a corepresentation of the third type. The combinatorial structure appears in diagram (14):

\[
\begin{array}{ccc}
M & U & L \\
\vdots & \vdots & \vdots \\
\psi_- & \psi_+ & -i \\
\end{array}
\]

(14)

\[\hat{Q}_{6,p}^3 \psi_l(k) = e^{-i\pi \frac{1}{5}} e^{-i k_z \frac{3}{5}} \psi_l(k) \quad \text{with } l \in \{1, 3, 5\} \] (16)

with \( P_6 \) and \( T \) commute we know that

The isotropy groups of the points K and H are generated by \( Q_{6,p}^2 \) and \( Q_{6,p}^3 T \) while the isotropy group of the path K-H between the points is only generated by \( Q_{6,p}^3 \). Since \( \hat{Q}_{6,p}^3 = -e^{-ik_z} \) we may diagonalise this operator on the path K-H having eigenvalues

\[\hat{Q}_{6,p}^3 \psi_l(K) = e^{-i\pi \frac{1}{5}} \psi_l(K), \quad \hat{Q}_{6,p}^3 \psi_l(H) = e^{-i\pi \frac{1}{3}} \psi_l(H).\] (17)
\((Q_{6,p}^3)^2 = e^{-k_x p}\) and therefore the antiunitary operator \(Q_{6,p}^3 T\) squares to 1 on \(K\) for any \(p\) and on \(H\) whenever \(p\) is even, and squares to -1 on \(H\) whenever \(p\) is odd; see equation (2).

On \(K\) the pair of representations \(\{\psi_1(K), \psi_5(K)\}\) define an irreducible corepresentation of the third type while \(\psi_3(K)\) defines a corepresentation of the first type. Note that Kramer’s degeneracy rule does not apply to the state \(\psi_3(K)\) since the antiunitary operator \(Q_{6,p}^3 T\) squares to 1 on \(K\).

On \(H\) the relations of the representations depend on \(p\). For \(p = 1\) we have that \(Q_{6,p}^3 T\) squares to -1 and all the states come in pairs. The pair \(\{\psi_3(H), \psi_5(H)\}\) defines a corepresentation of the third type while \(\psi_1(H) \oplus \psi_1(H)\) defines a corepresentation of the second type. The combinatorial structure appears in diagram (17).

\[
K \quad P \quad H \quad (17)
\]

The minimal set of compatibility relations from BCS is:

\[
K_1(1) \rightarrow P_1(1) \quad P_1(1) \oplus P_2(1) \leftarrow H_1 H_3(2)
\]
\[
K_2 K_3(2) \rightarrow P_2(1) \oplus P_3(1) \quad 2P_3(1) \leftarrow H_2 H_3(2)
\]

which build into diagram (18). This agrees with diagram (19).

\[
K_1(1) \quad P_1(1) \quad H_2 H_3(2) \quad (18)
\]

For \(p = 2\) the operator \(Q_{6,p}^3 T\) squares to 1 on \(H\) and therefore we have that \(\{\psi_1(H), \psi_5(H)\}\) defines a corepresentation of the third type and \(\psi_3(H)\) defines a corepresentation of the first type. The combinatorial structure appears in diagram (19).

\[
K \quad P \quad H \quad (19)
\]

The minimal set of compatibility relations from BCS is:

\[
K_1(1) \rightarrow P_1(1) \quad P_1(1) \oplus P_3(1) \leftarrow H_2 H_3(2)
\]
\[
K_2 K_3(2) \rightarrow P_2(1) \oplus P_3(1) \quad P_1(1) \leftarrow H_1(2)
\]

which build into diagram (20). This agrees with diagram (19).

\[
K_1(1) \quad P_1(1) \quad H_2 H_3(2) \quad (20)
\]

\[
K_2 K_3(2) \quad P_2(1) \quad H_1(1)
\]

For \(p = 3\) the operator \(Q_{6,p}^3 T\) squares to -1 and therefore the pair \(\{\psi_1(H), \psi_5(H)\}\) defines a corepresentation of the third type while \(\psi_3(H) \oplus \psi_3(H)\) defines a corepresentation of the second type. The combinatorial structure appears in diagram (21).

\[
K \quad P \quad H \quad (21)
\]

The minimal set of compatibility relations from BCS is:

\[
K_1(1) \rightarrow P_1(1) \quad P_2(1) \oplus P_3(1) \leftarrow H_2 H_3(2)
\]
\[
K_2 K_3(2) \rightarrow P_2(1) \oplus P_3(1) \quad 2P_3(1) \leftarrow H_1 H_3(2)
\]

which build into diagram (22) and agrees with diagram (21).

\[
K_2 K_3(2) \quad P_2(1) \quad H_2 H_3(2) \quad (22)
\]

\[
K_1(1) \quad P_1(1) \quad H_1 H_3(2)
\]

First principle calculations for hexagonal materials along the K-H path presented in Figure 4 recover the combinatorial structure of the electronic energy bands.

**Topological Band analysis on A-L-H and Γ-M-K planes**

The isotropy group of all cells besides the 0-cells on the A-L-H and Γ-M-K planes is the group of order two \(\langle T^3 \rangle\) generated by the antiunitary operator \(\hat{T}^3\).

Since \(\hat{T}\) and \(T\) commute we have that

\[
(\hat{T}^3)^2 = \hat{T}^6 T^2 = e^{-i p k_x}
\]

and therefore on the Γ-M-K plane and on the A-L-H plane whenever \(p\) is even we have \((\hat{T}^3)^2 = 1\) and on the A-L-H plane whenever \(p\) is odd we have \((\hat{T}^3)^2 = -1\).

The fact that \((\hat{T}^3)^2 = 1\) posses no restrictions on the possible representations of the energy bands along the plane Γ-M-K and on the plane A-L-H whenever \(p\) is even. Nevertheless, whenever \(p\) is odd, the fact that \((\hat{T}^3)^2 = -1\) on the plane A-L-H implies by Kramer’s
have the relations:

$$M(k_x, k_y, k_z) = (k_y, k_z, -k_x)$$

and the commuting relation with $Q$ is $MQM = Q^{-1}$. Once lifted as operators on the Hilbert space of states we have the relations:

$$\hat{M}^2 = -1, \quad \hat{M}\hat{Q}\hat{M}^{-1} = \hat{Q}^{-1} \quad \text{and} \quad (\hat{M}\hat{Q})^2 = -1,$$

which follow from the presence of SOC interaction.

**Topological band analysis on $\Gamma$-$A$**

On the $\Gamma$ and $A$ points, if $Q$ has an eigenvector $\psi$ with eigenvalue $\lambda$ then $\hat{M}$ is an eigenvector of $Q$ with eigenvalue $\lambda^{-1}$. Since the order of $Q$ on $\Gamma$ and $A$ is finite, then $|\lambda| = 1$ and therefore $\lambda^{-1} = \overline{\lambda}$. Hence we have that the irreducible representations of $\langle \hat{Q}, \hat{M} \rangle$ are of the form

$$\hat{Q} \mapsto \begin{pmatrix} \lambda & 0 \\ 0 & \lambda^{-1} \end{pmatrix}, \quad \hat{M} \mapsto \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

where $\lambda$ is an appropriate root of unity. These representations lift to corepresentations to the group $\langle \hat{Q}, \hat{M}, T \rangle$ by assigning to the operator $\hat{M}T$, which squares to 1, the operator of complex conjugation $\overline{\hat{M}}$. Note that this choice is coherent since

$$(\hat{M}T)\hat{Q}(\hat{M}T)^{-1} = \hat{Q}^{-1} \quad \text{and} \quad (\hat{M}T)^{-1}\hat{M}(\hat{M}T) = \overline{\hat{M}},$$

and $\overline{\hat{M}}$ flips the eigenvalues of $\hat{Q}$ and commutes with the matrix associated to $\overline{\hat{M}}$.

Whenever $\lambda$ is not a real number, the irreducible corepresentations of the group $\langle \hat{Q}, \hat{M}, T \rangle$ are of the first kind, all of them are 2-dimensional and the eigenvalues of $\hat{Q}$ on these corepresentations are the roots of unity $\lambda$ and $\overline{\lambda}$. The restriction of these corepresentations to the group $\langle \hat{Q}, T \rangle$ become the corepresentations of the third type that were described in the analysis of the band diagram that appears in [4].

Whenever $\lambda$ is real the operator $\hat{Q}$ commutes with $\overline{\hat{M}}$, therefore the irreducible corepresentations are of the first kind. Restricting these corepresentations to $\langle \hat{Q}, T \rangle$ we obtain the representations of the second type that were described in the analysis of the band diagram that appears in [4].

Now, on the $\Gamma$-$A$ path the isotropy group is $\langle \hat{Q}, \overline{\hat{M}} \rangle$. Hence the 1-dimensional representations of $\hat{Q}$ that appear in equation [3] lift to corepresentations of $\langle \hat{Q}, \overline{\hat{M}} \hat{T} \rangle$ by assigning to $\overline{\hat{M}}\hat{T}$ the operator of complex conjugation $\overline{\hat{M}}$. Therefore on the path $\Gamma$-$A$ the description of the eigenvectors of $\hat{Q}$ given in equation [3] works for the groups $P6_p^{22}$ as well.

We conclude that the maximal band representations for the groups $P6_{1}^{22}$, $P6_{2}^{22}$ and $P6_{3}^{22}$ along the path $\Gamma$-$A$ are the same as the ones the appear in figures [4], [6] and [8] respectively.

First-principle calculations for hexagonal materials with $P6_p^{22}$ space group symmetry presented in Figure 5 recover the combinatorial structure of the bands shown in [4], [6] and [8]. We can notice the formation of Weyl points in the accordion-like (Figure 5a) and hourglass-like dispersion (Figure 5b and c), which are protected by 6-fold screw rotation symmetry.

**Symmetry groups $P6_p^{22}$**

Whenever we compare the band representations of the symmetry groups $P6_p^{22}$ and $P6_p$ along the vertical 1-cells of the Brillouin zone something quite interesting happens. It turns out that all minimal band representations along the vertical lines $\Gamma$-$A$, $M$-$L$, and $K$-$H$ for the symmetry groups $P6_p^{22}$ are isomorphic to the minimal band representations for the symmetry groups $P6_p$.

This interesting phenomenon is explained as follows. The irreducible corepresentations for the groups $P6_p^{22}$ along the vertical paths restrict to the irreducible corepresentations for the groups $P6_p$ once the symmetry $M$ is forgotten. This restriction map is one-to-one and onto. Let us see with more detail this assertion.

The groups $P6_p^{22}$ are obtained by adding to the groups $P6_p$ a $180^\circ$-degrees rotation along a specific axis; see [1]. In momentum space, these rotations behave as the operator

$$\hat{M}(k_x, k_y, k_z) = (k_y, k_z, -k_x)$$

and the commuting relation with $Q$ is $\hat{M}Q\hat{M}^{-1} = Q^{-1}$. Once lifted as operators on the Hilbert space of states we have the relations:

$$\hat{M}^2 = -1, \quad \hat{M}\hat{Q}\hat{M}^{-1} = \hat{Q}^{-1} \quad \text{and} \quad (\hat{M}\hat{Q})^2 = -1,$$
The previous argument applies identically for the path M-L since we have that the isotropy group of M and L is \( \langle Q^3, \hat{M} Q, \hat{T} \rangle \) with \((\hat{M} \hat{Q})^2 = -1 \) and \((\hat{M} \hat{Q}) \hat{Q}^3 (\hat{M} \hat{Q})^{-1} = \hat{Q}^{-3}\). Hence the operator \( \hat{M} \hat{Q} \) plays the role that \( \hat{M} \) played in the \( \Gamma \) and A points.

On the 1-cell M-L the isotropy group is \( \langle Q^3, \hat{T}Q^2 \hat{M} \rangle \) and note that \((\hat{T}Q^2 \hat{M})^2 = 1 \) and that \((\hat{T}Q^2 \hat{M}) \hat{T}Q^3 \hat{Q}(\hat{T}Q^2 \hat{M}) = \hat{Q}^{-3}\). Therefore the 1-dimensional representations of \( Q^3 \) defined for the group \( P_{6p} \) on M-L in equation \( \text{(10)} \) lift as one-dimensional corepresentations of the group \( \langle Q^3, \hat{T}Q^2 \hat{M} \rangle \) whenever we represent the operator \( \hat{T}Q^2 \hat{M} \) as the complex conjugation \( \hat{K} \).

Hence the maximal band representations for the groups \( P6_122, P6_222 \) and \( P3_2 \) along the 1-cell M-L are the same as the ones the appear in figures \( \text{(11)}, \text{(14)} \) and \( \text{(12)} \) respectively.

Electronic band structure for \( P6_222 \) materials along the M-L path presented in Figure 6 recover the combinatorial structures of the energy bands. From Figures 6a and 6c, we can see the formation of Weyl points with hourglass-like dispersion given by the relations presented in diagrams \( \text{(11)}, \text{(12)} \).

**Topological band analysis on K-P-H**

The isotropy groups for K and H are generated by \( \hat{Q}^2, \hat{M} \) and \( \hat{T}Q^3 \). On K we know that \((\hat{Q}^3 \hat{T})^2 = 1 \) with

\[
(\hat{Q}^3 \hat{T}) \hat{M} (\hat{Q}^3 \hat{T}) = \hat{M}^{-1} \quad \text{and} \quad (\hat{Q}^3 \hat{T}) \hat{Q}^2 (\hat{Q}^3 \hat{T}) = \hat{Q}^2.
\]

Whenever the eigenvalues of \( \hat{Q} \) in equation \( \text{(10)} \) are not real, the 2-dimensional representation of \( \langle \hat{Q}^3, \hat{Q}^3 \hat{T} \rangle \) lifts to a representation of \( \langle \hat{Q}^2, \hat{M}, \hat{Q}^3 \hat{T} \rangle \) as it was done before. Whenever the eigenvalue of \( \hat{Q} \) is real, the 1-dimensional representation of \( \langle \hat{Q}^2, \hat{Q}^3 \hat{T} \rangle \) may be lifted to one in \( \langle \hat{Q}^3, \hat{M}, \hat{Q}^3 \hat{T} \rangle \) by assigning either \( i \) or \( -i \) as eigenvalue for \( \hat{M} \) and by representing the operator \( \hat{Q}^3 \hat{T} \) by complex conjugation \( \hat{K} \).

On the point H whenever \( p \) is odd the operator \( \hat{Q}^3 \hat{T} \) squares to -1. Therefore all 2-dimensional irreducible corepresentations of \( \langle \hat{Q}^2, \hat{Q}^3 \hat{T} \rangle \) lift to 2-dimensional irreducible corepresentations of the group \( \langle \hat{Q}^2, \hat{M}, \hat{Q}^3 \hat{T} \rangle \) as it was done above. Whenever \( p \) is even the same argument as in the case of the point K can be carried out and the 1-dimensional corepresentations that appear lift to 1-dimensional representations of the group \( \langle \hat{Q}^2, \hat{Q}^3 \hat{T} \rangle \).

We conclude that the maximal band representations for the groups \( P6_122, P6_222 \) and \( P3_2 \) along the 1-cell K-P-H are the same as the ones they appear in figures \( \text{(17)}, \text{(19)} \) and \( \text{(21)} \), respectively. Here it is worth pointing out that the maximal band representation along the K-H line for the groups \( P6_122 \) may appear in the shape of the following diagram:

\[
\begin{array}{cccc}
K & P & H \\
\end{array}
\]

The open ends on the side of the K-point share the eigenvalue of -1 for the operator \( \hat{Q}^2 \) and have respectively \(+i\) and \(-i\) as eigenvalues for \( \hat{M} \). These points will be joined.
when they reach the \( \Gamma \)-point, hence they will tend to appear close to each other.

First-principle calculations for \( P6_322 \) materials confirm the combinatorial structure of the energy bands along the K-H line as can be seen in Figure 7.

**Topological Band analysis on A-L-H and \( \Gamma-M-K \) planes**

The isotropy groups for the 1-cells on these planes consist of the groups \( \langle \hat{Q}^{3T}, \hat{Q} \hat{M} \rangle, \langle \hat{Q}^{3T}, \hat{M} \rangle \) and \( \langle \hat{Q}^{3T}, \hat{Q}^3 \hat{M} \rangle \). The unitary operators \( \hat{M}, \hat{Q} \hat{M} \) and \( \hat{Q}^3 \hat{M} \) square to -1 and their relation to the antiunitary operator \( \hat{Q}^{3T} \) is the following. On the \( \Gamma-M-K \) plane, and on the A-L-H plane whenever \( p \) is even, we know that \( (\hat{Q}^{3T})^2 = 1 \) and

\[
(\hat{Q}^{3T})\hat{Q}^a \hat{M} (\hat{Q}^{3T})^{-1} = (\hat{Q}^a \hat{M})^{-1}.
\]

Therefore the irreducible corepresentations are of the first type and of dimension 1 in this case.

On the A-L-H plane whenever \( p \) is odd the antiunitary operator obeys the equation \( (\hat{Q}^{3T})^2 = -1 \) and it commutes with the operators \( \hat{Q}^a \hat{M}, \) i.e.

\[
(\hat{Q}^{3T})\hat{Q}^a \hat{M} (\hat{Q}^{3T})^{-1} = \hat{Q}^a \hat{M}.
\]

Therefore the irreducible corepresentations are of the third type and of dimension 2, and all energy bands on the 1-cells A-L, L-H and A-H are degenerate with degeneracy of degree 2.

This could be observed on the energy bands of the materials \( \text{AgF}_3 \) and \( \text{AuF}_3 \) (\( P6_322 \) #178) in Figure 8 and \( \text{CoNb}_3\text{S}_6 \) (\( P6_322 \) #182) in Figure 10 where the energy bands along the \( \Gamma-M, M-K \) and \( \Gamma-K \) paths are non-degenerate and along the paths A-L, L-H and A-H are degenerate of degree 2.

**Complete combinatorial band structure**

We may assemble the combinatorial diagrams described previously thus having a complete topological band structure. There are several ways to assemble the diagrams previously described and in what follows we will present some complete topological models that appear in the electronic band structure of the materials with the prescribed symmetry.

For the symmetry groups \( P6_3 \) and \( P6_322 \) we may assemble the topological band structure as it is shown in the following diagram:

![Diagram](image)

This structure could be seen on the twelve bands above the Fermi level in the material \( \text{AgF}_3 \) and it almost captures the complete electronic structure on the conduction bands in the material \( \text{AuF}_3 \) as it is shown in Figure 8.

The difference that appears on the bands of \( \text{AuF}_3 \) is due to the strong spin-orbit coupling interaction of the material. This allows other combinations for the ways on which the bands assemble along the M-L path.

In the case of the symmetry group \( P6_3 \) the combinatorial structure of the energy bands can be assembled as described in the following diagram:

![Diagram](image)

This combinatorial structure could be seen on the eight bands below the Fermi level in the material \( \text{PL}_3 \) as it is shown in Figure 9. At least two features make this combinatorial structure very interesting, the superposition of the hourglass energy bands along the \( \Gamma-A \) path and the way the energy bands are joined on the K point. These features cannot be deduced from the corepresentations of the isotropy groups nor the combinatorial structure along the edges of the Brillouin zone. This is just one of the possible ways that the topological energy bands may be assembled.

The topological assembly of the energy bands for the symmetry group \( P6_322 \) is more elaborate. It may require
FIG. 8. (a) Lower part of the conduction band structure for AgF\textsubscript{3} with the combinatorial structure described in diagram (24). (b) Lower part of the conduction band structure for AuF\textsubscript{3} with almost identical combinatorial structure as AgF\textsubscript{3}. Calculated topological chiralities (+1, 0 or -1) are indicated close to the Weyl points.

FIG. 9. Electronic band structure for PI\textsubscript{3} (P6\textsubscript{3} space group) with the combinatorial structure described in diagram (25).

as much as 20 energy bands as it can be seen in the electronic band structure of CoNb\textsubscript{3}S\textsubscript{6} that appears in Figure 10. The complete combinatorial diagram will not be included in this work.

MATERIALS REALISATION

We have used the materials project database \[29\] and AFLOW database \[30\] in order to show examples of materials for each of the space groups studied in the topological analysis. We have chosen materials with nonsymmetric space groups generated by a 6-fold rotation symmetry with \(p\)-screw symmetry operation. Moreover, we have compared these materials with the ones whose symmetry groups also include two extra symmetries of 2-fold rotation axis around of axis which is perpendicular to the main \(z\)-axis (P6\textsubscript{p}, 22 space groups).

The materials used as examples for the prediction of the electronic band structure were: In\textsubscript{2}Se\textsubscript{3}, KCaNd(PO\textsubscript{4})\textsubscript{2}, PI\textsubscript{3}, AgF\textsubscript{3}, AuF\textsubscript{3}, TaGe\textsubscript{2} and Nb\textsubscript{3}CoS\textsubscript{6}.

For P6\textsubscript{1} (#169) we have used the compound indium selenide (In\textsubscript{2}Se\textsubscript{3}) in the \(\gamma\)-phase, which is called “defect wurtzite structure” and it is a common crystal structure for In\textsubscript{2}Se\textsubscript{3} thin-film epitaxial growth. In\textsubscript{2}Se\textsubscript{3} is a direct semiconductor with a bandgap energy of around 1.0 eV and potential application in photovoltaic devices \[31\].

P6\textsubscript{2} (#171) is not a common space group for the solid-state phase of normal materials. Instead we have used the space group P6\textsubscript{4} (#172) which is band electronic topological equivalent to P6\textsubscript{2}. For P6\textsubscript{4} (#172) we have used the double phosphate KCaNd(PO\textsubscript{4})\textsubscript{2} which is isotypic with the hexagonal phase of LaPO\textsubscript{4}. KCaNd(PO\textsubscript{4})\textsubscript{2} is an insulator material with a bandgap energy of \(\sim 4.5\) eV which could be used in optoelectronic devices and white-light-emitting diodes when it is doped with transition-metal or rare-earth elements \[32\].

For the P6\textsubscript{3} (#173) space group we have used the phosphorus triiodide PI\textsubscript{3} which is an indirect semiconductor material (\(\sim 2.0\) eV) with valence band maximum at the \(K\)-point. The electronic band structure computed for PI\textsubscript{3} in Figure 9 shows the correspondence with the predicted group theory analysis presented in diagram (25). We can notice the formation of 2, 2 and 3 Weyl points between the \(k\)-lines L-M, \(\Gamma\)-A, H-K respectively. These Weyl points are symmetry protected by the 6-fold screw symmetry.

For the P6\textsubscript{3} (#173) space group we have used the phosphorus triiodide PI\textsubscript{3} which is an indirect semiconductor material (\(\sim 2.0\) eV) with valence band maximum at the \(K\)-point. The electronic band structure computed for PI\textsubscript{3} in Figure 9 shows the correspondence with the predicted group theory analysis presented in diagram (25). We can notice the formation of 2, 2 and 3 Weyl points between the \(k\)-lines L-M, \(\Gamma\)-A, H-K respectively. These Weyl points are symmetry protected by the 6-fold screw symmetry. We also notice a special energy crossing on the \(K\)-point which is characteristic of 6-fold symmetry.
systems like graphene and silicene. This crossing is predicted by the group theory analysis in diagram (25) as one of the possible ways the topological bands assemble.

The space group P6\textsubscript{1}22 (#178) is a common space group for trifluoride materials. Two of the materials are AgF\textsubscript{3} and AuF\textsubscript{3} which have an interesting band structure topology as it is shown in Figure 8. It is worth noting that in this case a complete topological band structure was determined in diagram (24) from the band analysis carried out in the previous section. We can note an accordion-like dispersion in the Γ-A path (see Figure 5), which produces at least five crossings along this k-path four of them Weyl points. The evolution of these 12 bands along the high symmetry lines produces 3 and 4 symmetry protected Weyl points at the L-M and K-H paths respectively (see Figures 6 and 7).

For the case of P6\textsubscript{3}22 (#180) space group, we have studied the tantalum germicide (TaGe\textsubscript{2}) material which is an intermetallic compound with 12 symmetry operations and a band structure with Weyl points as presented in Figures 5, 6 and 7. The electronic band structure in Figure 5 shows hourglass-like Weyl points in the Γ-A path which are protected by the nonsymmorphic screw symmetry.

Finally, we have used as an example for the P6\textsubscript{3}22 (#182) space group the material Nb\textsubscript{3}CoS\textsubscript{6}, which is a quasi-two-dimensional material with Co atoms inserted between Nb-S layers. It makes a sandwich structure in the sequence of Co-SNbS-Co and its unit cell is one of an hexagonal lattice. Moreover, the Co atoms are localised in a chiral position on the z-axis thus producing a nonsymmorphic screw symmetry (C\textsubscript{2} rotation plus T\textsubscript{a/2} partial translation) for this compound. The electronic band crossings for CoNb\textsubscript{3}S\textsubscript{6} including SOC interaction are shown in Figure 10 where we can see the formation of hourglass-like dispersion on the Γ-A and L-M paths at different energies. In particular it is noted that the material is a metal with hourglass dispersion at the Fermi energy. These particular energy crossings are protected by the time-reversal and screw symmetry of the CoNb\textsubscript{3}S\textsubscript{6} material. We can also see the formation of nodal lines around the Γ-point on the k\textsubscript{z}=0 plane, which is due to the band crossings at the Fermi level on the K-Γ-M path (see Figure 10).

For the six materials described above we have carried out first-principles calculations and we have reproduced the predicted crossing points on the energy bands according to each space group symmetry.

In order to study the electronic band structure for the P6\textsubscript{p} and P6\textsubscript{3}22 hexagonal materials, we have carried out first-principles calculations within the density-functional theory (DFT) framework. Exchange and correlation effects were treated with generalized gradient approximation (GGA) as implemented in the Vienna ab-initio simulation package (VASP). The calculations of spin-orbit coupling (SOC) interaction were included self-consistently at the DFT level. Electron wave function was expanded in plane waves up to cut-off energy of 500 eV and a grid of 0.02 (2\pi/Å) k-space resolution has been used to sample the first Brillouin zone (FBZ). For the hexagonal materials, we have used FINDSYM code to determine the correct crystal symmetry operations. As it is shown in Figures 2 and 11(a) we have found full agreement between the different theoretical approaches to the band structure calculation. Moreover, we have studied physics beyond the topological band crossings using the Wannier representation generated by the Wannier interpolation technique. We have used the Wanniertools package in order to calculate the position and chirality (by using the Wilson-loop method) of possible Weyl points for the P6\textsubscript{3}22 space group. We also calculated the Berry curvature, the k-resolved (240 \textsuperscript{3} k-mesh) anomalous Hall conductivity and the spin Hall conductivity in order to clarify the contribution of selected Weyl points in the magneto-transport properties of these hexagonal materials.

**WEYL POINTS IN THE P6\textsubscript{3}22 SPACE GROUPS**

Weyl points were observed in the six materials described above due to the screw symmetry presented in the P6\textsubscript{p} and P6\textsubscript{3}22 space groups. However, we have chosen particular example materials AgF\textsubscript{3} and AuF\textsubscript{3} (P6\textsubscript{3}22) in order to show a detailed topological analysis of the energy band crossings.

**Weyl points in AgF\textsubscript{3}**

The electronic band structure for this material below the Fermi level is shown in Figure 11(a), where it is shown also the value of the chirality (+1 and -1) for the Weyl points close to the maximum of the valence band energy. From Figure 11(a) we note that close to the valence band maximum (0 eV) it is possible to find three different Weyl points near in energy with values of 0.22, -0.28 and -0.27 eV (dotted lines in Figure 11(a)). These nodes live along the k\textsubscript{z}-paths Γ-A, K-H, and M-L and they have also similar k\textsubscript{z} components 0.44, 0.46, and 0.41 respectively (in fractional coordinates of the k\textsubscript{z}-line). In particular, we have calculated the position of these nodal points using a gradient conjugate technique in the full FBZ and these locations are consistent with the group theoretical predictions.

In the three-dimensional torus defined by the translational symmetries, there are 2 Weyl points of chirality +1 induced by the Weyl point along the Γ-A path, 6 points of chirality +1 induced by the Weyl point along the M-L path and 4 points of chirality -1 induced by the Weyl point along the K-H path (See Figure 8). The
FIG. 11. (a) Valence band structure and chirality for the three Weyl points shown between the high-symmetry $k$-lines (L-M, Γ-A, H-K) of the BZ, (b) integration of the $xy$-component of Berry curvature ($\Omega_{xy}$) on the $k_z$-positive ($\alpha^+$) and $k_z$-negative ($\alpha^-$) regions of the irreducible first BZ as a function of energy, (c) $\sigma_{xz}$ and $\sigma_{yz}$ components of the spin Hall conductivity tensor as a function of energy, (d) $\log(|\Omega_{xy}| + 1)$ on the $k$-plane touching the three Weyl points, and (e) top view of the Berry curvature field on the $k$-plane touching the three Weyl points for AgF$_3$ in the $P6_122$ space group. Here M, Γ, and K represent the location of Weyl points at the $k_z$-lines L-M, Γ-A, and H-K respectively. M and Γ are sources (+1 chirality) while K is a sink (-1 chirality). The Fermi level is set to zero. The sum $2 + 6 - 4$ of those chiralities is not zero and it is equal to +4. Hence, by the cancellation of right and left chiralities in the exclusive presence of Weyl points proven in [10], we know that there should exist Weyl points outside the 1-dimensional cells whose chiralities add to −4. But any Weyl point that exists outside the 1-dimensional cells must appear a multiple of 12 times since the 2-dimensional cells have multiplicity 12 and the 3-dimensional cell has multiplicity 24 as we have shown in the Table I. Clearly this is not possible since −4 is not multiple of 12. Therefore the fact that the chiralities of the three Weyl points add to 4 implies the existence of a Weyl nodal line in the AgF$_3$ bulk material. And indeed this is the case. We have checked the existence of nodal lines which are small circles that appear very close to the Weyl points along the M-L path with an energy level of -0.27 eV. Figure 11(d) shows a considerable contribution to the Berry curvature near point M (M-L path) which is due to the presence of a nodal line close to M-L Weyl point.

In order to check the local manifestation of the geometric properties of the wave-functions in $k$-space, we have calculated the $xy$-component of the Berry curvature ($\Omega_{xy}$) on the $k$-plane that defines these three Weyl points as it is shown in Figure 11(d). We can see a large contribution of the Berry curvature near degeneracy points, where M, Γ, and K represent the location of Weyl points at the $k_z$-lines L-M, Γ-A, and H-K respectively. In addition, the Berry curvature field indicates that of these Weyl points Γ and M act as ‘sources’ and K as ‘sink’ of the magnetic field in the momentum space (Figure 11(e)). These topological monopole charges are located at the (degenerate) band crossings and their signs are consistent with the chirality calculated $\chi_+ = +1$ for Γ-A and M-L and $\chi_- = -1$ for K-H (see Figure 11(a)). These Weyl points are protected by the nonsymmorphic crystal symmetry and time-reversal symmetry presented in the AgF$_3$ ($P6_122$) material. These points are near to the valence band maximum (around 250 meV) and they could be reached with a strong $p$-doping of this semiconductor material.

On the other hand, the integration of the $xy$-component of Berry curvature ($\Omega_{xy}$) on the $k_z$-positive ($\alpha^+$) and $k_z$-negative ($\alpha^-$) regions of the first BZ as a
function of energy is shown in figure 11(b). We found a high partial contribution to the anomalous Hall conductance (AHC) due to the K-H Weyl points (around -0.28 eV in energy) even though the total AHC is zero due to time-reversal symmetry (the positive $\alpha^+$ and negative $\alpha^-$ integration on the full FBZ cancel). This phenomenon could be understood due to different chirality values of the Weyl points close to the M-L and K-H lines, thus increasing and decreasing the AHC in a small range of energy. It is known that positive and negative peaks on the electrical Hall conductivities can be sources of considerable large spin Hall conductivity (SHC) [39]. We found that the total integral of the spin Hall curvature, which is even in TRS, is not zero and its huge contribution can be attributed to the presence of Weyl points in the valence band. From Figure 11(c) we can see a large value for the spin Hall conductivity (SHC) of around 600 $(h/e)(S/cm)$, far larger than the one of the pure element Ag which around 100 $(h/e)(S/cm)$ [40]. This results are in complete agreement with the crystal symmetry analysis for the full SHC tensor for the $P6_322$ space group, on which the $\sigma_{xy}^z$ ($-\sigma_{yx}^z$) is not zero [11]. Therefore we propose that $\text{AgF}_3$ can exhibit a large intrinsic spin Hall effect (SHE) mainly due to the particular contribution of the Weyl points to the spin-dependent Berry curvature. The energy dependence of the spin Hall conductivity can be tuned in order to electrically generate or detect spin currents in spintronic devices.

**Weyl points in AuF$_3$**

Weyl points were also analysed in the AuF$_3$ material, which crystallises at the $P6_322$ space group. The valence band structure for this material is shown in Figure 12(a) where it is also shown the value of the topological charges (chiralities of +1) for the three Weyl points (at the $\Gamma$-A, K-H and M-L lines) generated by the last valence bands. We can notice that the net chirality of these three points is +12 due to the fact that they must be counted twice, four-times and six-times at $\Gamma$-A, K-H and M-L respectively (these are the multiplicities of the 1-cells that appear in Table 1). If only Weyl points were to be present, extra Weyl points with opposite chirality adding to -12 must be present in the bulk material in order for the total chirality to be zero. This is known as the Nielsen-Ninomiya theorem or fermion-doubling theorem [10].

In Figure 12(c) we calculated the $xy$-component of the Berry curvature ($\Omega_{xy}$) at different $k_z$-planes ($k_z$=0.268, 0.296 and 0.419) for the three Weyl points located at the high symmetry lines ( $\Gamma$-A, K-H and M-L lines). In Figure 12(c) we can also see three large contributions of the Berry curvature near to the K-point, these points are located at the plane $k_z$=0.415 (in fractional reciprocal lattice vectors). These three extra Weyl points have each a chirality of -1 and they are located on the KHLM-plane. Since the number of equivalent cells to the plane KHLM is 12, there are 12 Weyl points with negative chirality for a total contribution of -12. Therefore the net chirality (total topological charge) of all Weyl points in the Brillouin zone vanishes for the AuF$_3$ material as expected. We found that the AuF$_3$ (and AgF$_3$) satisfies the fermion doubling theorem incorporating Weyl points on the bulk.

In order to evidence the contribution of the topological states to spin transport properties of AuF$_3$, we have calculated the energy dependence of the spin Hall conductivity as it is shown in Figure 12(b). We can see a large value for the spin Hall conductivity of around 240 $(h/e)(S/cm)$ for the energy $E-E_F\sim 50$ meV, and it could increase to 550 $(h/e)(S/cm)$ for $E-E_F\sim 360$ meV. These values are larger than the one of the pure element Au which is around 40 $(h/e)(S/cm)$ [41]. This result indicates that the F element in the formation of the 4d transition-metal fluorides can increase the spin transport phenomena in pure 4d transition-metal elements. These findings may help in the quest for the use of Weyl nodes and SOC induced phenomena in developing next-generation of energy-efficient spintronics technology.

**Distribution of Weyl points and existence of Weyl nodal lines**

We have seen that the nonsymmmorphicity of the space groups $P6_3$ and $P6_{3}22$ implies the existence of Weyl points along the high symmetry lines $\Gamma$-A, $M$-$L$ and K-H. One could expect that the number of Weyl points between successive bands is optimal in the sense that the distribution of those Weyl points satisfies the Nielsen-Ninomiya theorem [10] of cancellation of right and left Weyl points and that the amount of Weyl points is minimal.

In the case of the space group $P6_322$ we have seen that the bands may assemble as shown in diagram 24 for the material $\text{AgF}_3$ and in a similar fashion in the material AuF$_3$. This assembly incorporates successive bands on which there are either three Weyl points or two Weyl points. In the former there is one Weyl point along $\Gamma$-A, one along M-L and one along K-H, and in the latter there is one Weyl point along $\Gamma$-A and the other is either along M-L or along K-H.

In the three dimensional torus defined by the translational symmetries the Weyl points along $\Gamma$-A appear twice, the Weyl points along K-H appear four times and the Weyl points along M-L appear six times (see Table 1). The topological constraint for the distribution of the Weyl points is given by the Nielsen-Ninomiya theorem which tells us that in the exclusive presence of Weyl points the total chirality is zero.

The only possible distribution of Weyl points including a Weyl point along the $\Gamma$-A path is when there are Weyl
FIG. 12. (a) Valence band structure for the material AuF$_3$ together with the chirality of the three Weyl points shown between the high-symmetry $k$-lines (L-M, Γ-A, H-K) of the BZ, (b) $\sigma^z_{yx}$ and $\sigma^z_{xy}$ components of the spin Hall conductivity tensor as a function of energy, (c) log(|$\Omega_{xy}$| + 1) on different $k_z$-planes (0.268, 0.296, 0.415 and 0.419) where the Weyl points are located in AuF$_3$. Here M, Γ and K represent the location of Weyl points at the $k_z$-lines L-M, Γ-A and H-K respectively. M, K and Γ are sources (+1 chirality) while the three points close to K are sinks (-1 chirality). The Weyl point denoted by Γ appears 2 times, the one denoted by M appears 6 times and the one denoted by K appears 4 times. These 12 Weyl points with positive chirality cancel with the 12 Weyl points with negative chirality induced by the three Weyl points close to the one denoted by K. The Fermi level is set to zero.

In the case that the chiralities along Γ-A, M-L and K-H are equal, their chiralities would add up to 12. Therefore there could be a Weyl point in any high-symmetry plane (2-cell) since all these planes appear 12 times in the three-dimensional Brillouin zone (see Table I). This is indeed the case in the valence bands of AuF$_3$ shown in Figure 12 where there is a Weyl point with −1 chirality in the KHLM plane ($k_z = 0.415$) with multiplicity 12. It is also the case on the second and third conduction bands of AuF$_3$ shown in Figure 8 where there is a Weyl point with +1 chirality in the ΓKHA plane ($k_z = 0.212$) with multiplicity 12.

On the second and third conduction bands of AgF$_3$, something very interesting happens. The chiralities along Γ-A, M-L and K-H add up to −12 (see Figure 8) but the distribution of Weyl points is more elaborate. In Table II we have shown the location of the Weyl points as well as their chiralities. It is worth pointing out that there are double-Weyl points with +2 chiralities along the Γ-K path and that the total number of Weyl points is 66 with a net-zero chirality.

In the case that the chiralities along Γ-A, M-L and K-H have not the same sign, as it is the case for the valence bands of AgF$_3$ shown in Figure 11(a), we have that the sum of the chiralities is less than 12. In this case, there is no distribution of exclusive Weyl points that satisfies the Nielsen-Ninomiya theorem since any Weyl point on the high-symmetry planes appears 12 times and any Weyl point on the 3-dimensional BZ appears 24 times.
TABLE II. Distribution of Weyl points for the second and third conduction bands in AgF$_3$. The cell denotes the high symmetry line or plane where the points are located, the momentum coordinates $k_1, k_2, k_3$ are given in fractions of the hexagonal reciprocal coordinates, $E$ denotes the energy (in eV), $\chi$ the chirality, #-cells the multiplicity of the cell and Tot. the total contribution in chirality. There are 66 Weyl points in total, 24 with +1 chirality, 36 with −1 chirality and 6 with +2 chirality. The total chirality is zero.

| Cell | $k_1$  | $k_2$  | $k_3$  | $E$     | $\chi$ | #-cells | Tot. |
|------|--------|--------|--------|---------|--------|---------|------|
| ΓA   | 0      | 0      | 0.454  | 0.487   | −1     | 2       | −2   |
| KH   | 0.333  | 0.333  | 0.227  | 0.372   | −1     | 4       | −4   |
| ML   | 0      | 0.5    | 0.408  | 0.333   | −1     | 6       | −6   |
| ΓK   | 0.227  | 0.227  | 0      | 0.412   | +2     | 6       | +12  |
| ΓKM  | 0.256  | 0.306  | 0      | 0.368   | −1     | 12      | −12  |
| ΓKHA | 0.313  | 0.313  | 0.271  | 0.372   | +1     | 12      | +12  |
| ΓKHA | 0.227  | 0.227  | 0.473  | 0.421   | +1     | 12      | +12  |
| ΓMLA | 0      | 0.325  | 0.496  | 0.434   | −1     | 12      | −12  |

(see Table I). We infer that whenever the sum of the chiralities along the high symmetry lines is not a multiple of 12 then there must exist Weyl nodal lines on the bulk. This is the case for the valence bands of AgF$_3$ as we have seen before.

The same criterion applies whenever there is a Weyl point along the Γ-A path and another either along M-L or along K-H. In these cases the net chirality add up $\pm 2$, $\pm 4$, $\pm 6$ or $\pm 8$. Since there are no more Weyl points located in the high-symmetry lines (1-cells), there is no $k$-space distribution of Weyl points in the 3-dimensional BZ that satisfies the Nielsen-Ninomiya theorem; the multiplicities of the Weyl points along the high-symmetry planes and 3-dimensional BZ are multiples of 12 (see Table I). Therefore we infer the presence of Weyl nodal lines in all these cases. Examples of the presence of nodal lines following the previous argument was also found on the fourth and fifth and the sixth and seventh conduction bands in AgF$_3$ and AuF$_3$ and on the eighth and ninth conduction bands of AgF$_3$ as can be noted in Figure 5.

Let us finish by noting that the Weyl points do not necessarily appear in pairs of opposite chirality. In materials with nonsymmorphic hexagonal symmetry with inversion symmetry breaking, the distribution of Weyl points must obey the Nielsen-Ninomiya theorem and also must be counted as many times as the multiplicity of the cell on which they appear. These conditions break the symmetry under which Weyl points appear in pairs of opposite chirality. In this work, we have shown many instances on which this is the case. This feature has been also noted in [12] where topological charge of Weyl phonons in nonsymmorphic trigonal and hexagonal materials have been studied.

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In summary, we used topological corepresentation theory and connectivity group theory to predict Weyl points in nonsymmorphic hexagonal crystal structures. Weyl points appear at the high-symmetry lines with band crossings in accordion-like and hourglass-like dispersion relations. Both topology band analysis for hexagonal systems and first-principles calculations for real materials were used to corroborate the behaviour of the energy bands and the location of the Weyl points at the first Brillouin zone. These calculations show a complete agreement.

We also analysed the distribution of Weyl points in AgF$_3$ and AuF$_3$ materials. Taking into account that the number of times that a Weyl point appears on the Brillouin zone is precisely the multiplicity of the cell on which it appears, together with the Nielsen-Ninomiya theorem on the cancelation of left and right Weyl points, we find interesting distributions of the Weyl points in the valence and conduction bands of these materials. In particular, we show that the Weyl points in AgF$_3$ and AuF$_3$ materials do not appear in pairs of opposite chirality.

Our results show the simultaneous formation of Weyl points and nodal-lines in 4d transition-metal trifluorides such as AgF$_3$ and AuF$_3$. These materials are feasible Weyl-semimetal candidates with inversion symmetry breaking, with Weyl points protected by 6-fold screw and time-reversal symmetry. In addition, AgF$_3$ and AuF$_3$ exhibit a large intrinsic spin Hall effect (SHE) mainly due to the strong SOC interaction and the particular contribution of the Weyl points in the reciprocal space. These findings may help in the quest for the utilisation of Weyl points in developing next-generation of energy-efficient spin-based information technology.
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