Weyl fermions in ferromagnetic high-temperature phase of K$_2$Cr$_8$O$_{16}$

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Abstract

By combining first-principles calculations and symmetry arguments, we propose that the half-metallic phase of K$_2$Cr$_8$O$_{16}$ presents ferromagnetic Weyl fermions. In particular, K$_2$Cr$_8$O$_{16}$ possesses two pairs of Weyl nodes, which originate from two groups of nodal lines connected by the mirror reflection symmetry. We show that the non-trivial topological properties of K$_2$Cr$_8$O$_{16}$ come from the partially occupied t$_{2g}$ states of Cr, and we also demonstrate that such exotic topological feature is robust. The topological surface states and corresponding Fermi arcs are revealed. As K$_2$Cr$_8$O$_{16}$ is a realistic and widely studied material, our results suggest that K$_2$Cr$_8$O$_{16}$ is an ideal candidate for studying ferromagnetic Weyl fermions. In addition, K$_2$Cr$_8$O$_{16}$ possesses several interesting phenomena, such as the co-existence of charge density wave and Weyl fermions, even pairs of FM Weyl points, and tunable distribution of Weyl points, which will attract intensive attentions in this field.

In the past decades, exploring the materials that possess nontrivial topological electronic band structures is one of the central subjects in condensed matter physics [1–5]. Symmetry protected topological bulk states lead to nontrivial surface states which are important in both fundamental physics and potential applications. Plenty of candidates have been proposed, including not only gapped topological insulators [6–9], but also gapless topological semimetals, such as Dirac semimetals [10, 11], Weyl semimetals [12–14], and node-line semimetals [15–18]. Some of them have been observed in experiments [19–24].

Due to its exotic band structures coexisting with band topology and intrinsic magnetic orders, magnetic Weyl semimetals are expected to be applied in many fields such as quantum anomalous Hall effects [25] and current-driven magnetic textures [26]. However, the discovering of magnetic Weyl semimetals seems much slower than the non-magnetic ones. Although several magnetic candidates were theoretically proposed [12, 27–31], none of them have been confirmed in experiments, especially at room temperatures. Therefore, the identification of magnetic Weyl semimetals attracts intensive attentions.

K$_2$Cr$_8$O$_{16}$ is an important member of hollandite-type transition metal (HTM) oxides and has been studied both in theories and experiments [32–56]. It presents a ferromagnetic (FM) half-metallic state below 180 K through a paramagnetic-to-ferromagnetic transition. At 95 K, it undergoes a metal–insulator phase transition to an FM insulating state due to the Peierls type mechanism [47–51]. Thus, the Fermi surface nesting interplays with the unstable phonon modes through electron–phonon-coupling in its half-metallic phase. This behavior corresponds to the electrons of 3d orbitals. As a result, K$_2$Cr$_8$O$_{16}$
becomes a unique system, in which the Peierls transition couples the strong correlation effects while the FM order is maintained.

Beyond those interesting properties mentioned above, in this work we propose a half-metallic phase of K$_2$Cr$_8$O$_{16}$ in the range from 95 K to 180 K possessing ferromagnetic Weyl fermions. The topological properties originate from the partially occupied 3d orbitals in K$_2$Cr$_8$O$_{16}$, implying the crucial roles of the transition metal ions. Furthermore, we demonstrate that K$_2$Cr$_8$O$_{16}$ hosts even pairs of Weyl points under parity constraint, which is protected by the inversion symmetry [52]. The distribution of Weyl points in momentum space can be tuned by external magnetic fields.

The backbone structure of hollandite K$_2$Cr$_8$O$_{16}$ consists of edge-sharing CrO$_6$ octahedra, forming special double chains, in which oxygen atoms at the corner of octahedra are shared. The center of cross-section is occupied by K ions as it is visualized in figure 1(a). The tetravalent metal ions occupy the center of octahedra. The lattice of half-metallic K$_2$Cr$_8$O$_{16}$ belongs to I4/m space group (No. 87). According to our calculations, the optimized structure has lattice constants of $a = b = 9.93$ Å and $c = 3.00$ Å, which nicely fit experimental measurements [47, 53, 54]. The bulk Brillouin zone (BZ) and its two-dimensional (2D) BZ projected on the (010) and (001) surfaces are shown in figure 1(b). Our results confirm the FM half-metallic behavior of K$_2$Cr$_8$O$_{16}$, in which only the majority-spin electronic bands cross the Fermi level while the minority-spin bands have a sizable gap $\sim 3.5$ eV [see figure 2(a)]. The complete spin polarization around the Fermi level is originated from Cr atoms, contributed by the partially occupied $t_{2g}$ orbitals. The magnetic moment per Cr atom is 2.25 $\mu_B$, which agrees well with the experimental observations [55]. Furthermore, the band structure exhibits that the half-metallic state of K$_2$Cr$_8$O$_{16}$ addresses Fermi surface nesting in reciprocal space. As shown in figure 2(b), the nesting vector, referred to $k_n$, is along the $k_z$ direction, indicating the electronic instability. As it has been studied in recent years, this nesting feature is able to drive a Peierls type metal–insulator transition in K$_2$Cr$_8$O$_{16}$ [47–51].

Besides, when the effect of SOC is absent, there are topological non-trivial band-crossing points slightly above the Fermi level ($\sim 0.05$ eV) as shown in figure 2. These crossing points form two groups of continuous nodal line in reciprocal space. One is close to the plane of $k_z = \frac{\pi}{c}$ (not perfectly flat but with small fluctuations), while the other one is close to the plane of $k_z = -\frac{\pi}{c}$ [see figures 3(a) and (b)]. According to our analysis, the existence of these nodal lines in half-metallic K$_2$Cr$_8$O$_{16}$ is a consequence of symmetry protection. When the effect of SOC is ignored, the lattice of K$_2$Cr$_8$O$_{16}$ belongs to C$_{4h}$ point group. It contains spatial inversion symmetry $\mathcal{P}$ and mirror reflection symmetry $M_z$, where the reflection invariant plane is perpendicular to the $z$ axis. The two groups of nodal lines are respectively close to the planes of $k_z = \pm \frac{\pi}{c}$, which are connected by the mirror symmetry $M_z$ with respect to the reflection invariant plane of $k_z = 0$.

We next analyze the symmetry protection of the nodal line close to the plane of $k_z = \frac{\pi}{c}$, around the inverted center $N(0.5, 0.0, 0.0)$ in reciprocal space. The other one close to the plane of $k_z = -\frac{\pi}{c}$ follows the same mechanism. Generally, the two inverted bands can be described by the following two-band $k \cdot p$
Figure 2. Electronic band structures of half-metallic K$_2$Cr$_8$O$_{16}$ where the Fermi level is set to zero. The corresponding mapping of Fermi surface is shown in the right panels. The nesting vector $k_n$ is marked in red. (a) Spin-polarized band structures in the absence of SOC. The majority and minority spin states are denoted by blue and red lines, respectively. The region closes to one band crossing point (belongs to nodal line) is zoomed in the inset. The path from $K_1$ to $K_2$ is close to $k_z = \frac{\pi}{c}$ plane and passing through one point of nodal line (without SOC) and one Weyl point (with SOC). (b) Fermi surface without SOC. (c) Spin-polarized band structures by considering the effect of SOC. The direction of magnetization is set along the [010] direction. One of survived Weyl points is presented in the inset. (d) Fermi surface with SOC when it is magnetized along the [010] direction.

Hamiltonian:

$$\mathcal{H} = \sum_{i=1,2,3} d_i(k) \sigma_i$$

(1)

in which $d_i(k)$ are real functions, $k = (k_x, k_y, k_z)$ are components of the momentum, and $\sigma_i$ are the Pauli matrices. Here we ignore the kinetic term proportional to the identity matrix since it is irrelevant in studying the band crossing. The band inversion point $N$ in reciprocal space belongs to the little group of $C_i$ where only the spatial inversion symmetry $P$ is reserved. This condition constrains the Hamiltonian as

$$[\mathcal{H}, P] = 0,$$

(2)

which gives us

$$d_3(k) = d_3(-k) \quad \text{and} \quad d_{1,2}(k) = -d_{1,2}(-k).$$

(3)

Besides, in a spin-polarized system without SOC, the spins and orbitals are independent and two spin channels are decoupled. Thus, the conservation of spin leads to the spin orientation along an arbitrary direction. The bands belong to each single spin channel can be effectively considered as a spinless system only in terms of symmetries. In this case, the time-reversal (TR) operator $T$ is able to connect the majority and minority spin states with $T^2 = 1$, which gives another constrain condition of Hamiltonian:

$$[\mathcal{H}, T] = 0.$$

(4)

Hence, we have

$$d_2(k) = -d_2(-k) \quad \text{and} \quad d_{1,3}(k) = d_{1,3}(-k).$$

(5)

Equations (3) and (5) give $d_1(k) \equiv 0$. The rest two real functions $d_2(k)$ and $d_3(k)$, restricted by symmetry, can be expanded up to the second order as follows,
Figure 3. (a) The nodal lines in the absence of SOC in BZ are marked by red lines and the corresponding TRIM points are shown in blue. (b) The 2D projection of nodal lines (in red) along the [001] direction. The blue region is the 2D projection of the first BZ. (c) Two pairs of Weyl points in BZ in the presence of SOC with the [010] magnetization. These four Weyl points with opposite Chern numbers are differed by red and black dots. (d) The 2D projection of Weyl points along the [001] direction.

\[ d_2(k) = B_1 k_x + B_2 k_y + B_3 k_z, \]
\[ d_3(k) = C_0 + C_1 k_x^2 + C_2 k_y^2 + C_3 k_z^2, \]

and the energy eigenvalues of the Hamiltonian are

\[ E = \pm \sqrt{d_2(k)^2 + d_3(k)^2}. \]

The solution of band crossing requires \( d_2(k) = 0 \) and \( d_3(k) = 0 \). First, \( d_2(k) = 0 \) is a plane equation through the \( N \) point in reciprocal space. Second, the solution of \( d_3(k) = 0 \) is able to form an ellipsoidal surface (when \( C_0 < 0, C_1, C_2, \) and \( C_3 > 0 \)) or a hyperboloid surface (when \( C_0 \neq 0, \) one of \( C_1, C_2 \) and \( C_3 \) has opposite sign with the rest two). Consequently, the zero-energy mode solution of equation (7) is able to form a closed nodal ring or an open nodal line, respectively. The latter one fits our case of half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \), thus, the nodal line is protected by the co-existence of TR symmetry and spatial inversion symmetry.

This symmetry protection mechanism is suppressed in the presence of SOC, in which the coupling between spin and orbital degrees breaks the spin rotation symmetry. In other words, only spatial inversion symmetry is not able to protect any nodal line. Comparing figures 2(b) and (d), we can see that the SOC effect in half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \) just slightly modifies the profile of band structures while the Fermi surface nesting is preserved. Usually, according to the ideal model of Weyl semimetal, the Fermi surface degenerates to a group of discrete points in BZ, which is repulsive to Fermi surface nesting. However, in half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \), the corresponding bands possess weak dispersions along \( \text{Z} \rightarrow \text{P} \rightarrow \text{N} \rightarrow \text{Z}' \) lines as shown in figure 2. This feature implies strong modification for the shape of isoenergetic surface in a small energy region. Thus, the isoenergetic surface is able to quickly change from discrete points (at the energy of Weyl points) to a finite size by only shifting a small amount of energies. In other words, it allows Weyl points to exist slightly above the Fermi level (\(~0.02 \text{ eV}\) ). As a result, the accidental co-existence of Fermi surface nesting and Weyl
Fermions is present in a very small region above the Fermi level. Such exotic phenomenon has not been reported up to now.

The effect of SOC destroys the nodal line, and two pairs of Weyl points are present. Our studies show that the positions of Weyl points are away from the original nodal line [see the insets of figures 2(a) and (c)], which are centrosymmetric with respect to spatial inversion symmetry. Besides, the distribution of Weyl points significantly depends on the direction of magnetization, which is similar to some previous reported materials, such as \( \beta\)-\( \text{V}_2\text{OPO}_4 \) [30], \( \text{CrO}_2 \) [31], and magnetic Heusler alloys [56]. The anisotropy of system makes the different profiles of bands when changing magnetization directions. It is worth noting that the existence of two pairs of Weyl points is robust. In table 1, we list the reciprocal coordinates of Weyl points and the corresponding Chern number along different magnetization directions. We only list the coordinates for two of them, and the rest two are related to inversion symmetry with respect to the BZ center. It is worth mentioning that the two Weyl points, connected by spatial inversion symmetry, have the opposite sign of Chern numbers. From table 1, we can see these Weyl points are very close to the Fermi level in energy (\( \sim 0.02\text{ eV above} \)), which can be easily occupied by electrons at finite temperatures.

We notice that there are odd pairs of Weyl points in previously reported magnetic Weyl semimetals [30, 31, 56]. In contrast, we find two (even) pairs in half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \). This interesting feature can be understood from the view of parity eigenvalues [52]. In an FM system coexisting with inversion symmetry \( P \), one can define parities at time-reversal invariant momenta (TRIM) points. In a 2D case, the Chern number characterizes the topology by the product of the parities of all occupied bands at TRIM points. At this level, the state of a 3D system can be considered as an adiabatic evolution of 2D electronic wavefunction along the third direction perpendicular to the original 2D plane, e.g. the \( k_z \) direction.

In a nontrivial system, we accordingly have two cases. In the first one, the Chern numbers of the two sub-systems are taken into account, there will be 2(2\( n \)) pairs of Weyl points in the whole BZ. Our investigations indicate that the half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \) nicely fit the second case in which there are two planes with nontrivial Chern numbers in reciprocal space, \( C = 1|_{k_y=0} \) and \( C = 1|_{k_y=0.5} \), so the feature of two pairs of Weyl points is robust.

We notice that the magnetic anisotropic energy is below 1 meV per unit cell when the system is magnetized along different directions (see table 1). It has the lowest energy when it is magnetized along [100] and [010] directions. \( \text{K}_2\text{Cr}_8\text{O}_{16} \) was suggested as a soft magnet in the previous study [47]. Depending on the size of the magnetic domain, this feature might suggest the tunable distribution of Weyl points through external magnetic fields. Since the topological behavior essentially follows the same rule for

Table 1. The precise coordinates \((k_x, k_y, k_z)\) of Weyl points with corresponding Chern numbers and energies with respect to the Fermi level. For each direction of magnetization, only the coordinates of two Weyl points are listed while the rest two are related to the spatial inversion symmetry. The relative magnetic anisotropic energies per unit cell are listed in the last row where the energy of the [001] magnetization is taken as the reference.

| Direc. of M | \( k_x(2\pi/a) \) | \( k_y(2\pi/a) \) | \( k_z(2\pi/c) \) | \( E - E_F(eV) \) | Chirality | \( \Delta E(\text{meV}) \) |
|-----------|----------------|----------------|----------------|----------------|--------------|----------------|
| [001]     | 0.008          | 0.024          | 0.491          | 0.026          | -1           | 0.000         |
|           | 0.012          | 0.032          | -0.491         | 0.026          | 1            |
| [010]     | -0.247         | -0.039         | -0.491         | 0.019          | -1           | -0.266        |
|           | 0.247          | 0.040          | -0.491         | 0.019          | 1            |
| [100]     | -0.039         | 0.248          | -0.491         | 0.019          | -1           | -0.266        |
|           | 0.039          | -0.247         | -0.491         | 0.019          | 1            |
| [101]     | 0.054          | -0.174         | 0.491          | 0.023          | 1            | -0.140        |
|           | -0.016         | 0.170          | 0.490          | 0.022          | -1           |
| [110]     | -0.159         | -0.170         | 0.490          | 0.020          | -1           | -0.246        |
|           | 0.157          | 0.167          | 0.490          | 0.020          | 1            |
| [011]     | 0.171          | 0.018          | -0.490         | 0.023          | 1            | -0.140        |
|           | -0.175         | -0.052         | -0.491         | 0.021          | -1           |
| [111]     | -0.110         | -0.115         | 0.490          | 0.023          | -1           | -0.173        |
|           | 0.437          | 0.386          | 0.499          | 0.029          | 1            |
Figure 4. The surface band structures and corresponding Fermi arcs projected on the semi-infinite (010) surface. (a) Local density of states (LDOS). (b) The isoenergic surface with the energy of 0.019 eV above the Fermi level. The Fermi arcs connecting the projection of two Weyl points with opposite Chern numbers (in red and black) are clearly shown. The \( k \)-path of the LDOS is indicated by white dash lines in (b).

In summary, we propose that the half-metallic phase of \( \text{K}_2\text{Cr}_8\text{O}_{16} \) is a very important member in hollandite oxides, possesses the exotic topological Weyl fermions by performing first principles calculations. As a realistic half-metallic ferromagnet that has been experimentally synthesized for years, hollandite \( \text{K}_2\text{Cr}_8\text{O}_{16} \) can be considered as a promising candidate for future experimental studies of FM topological fermions. Our theoretical analysis shows that the half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \) presents nodal line type band structures in the absence of SOC. The nodal lines degenerate to two pairs of Weyl points when the effect of SOC is included. We have shown that the SOC effect just slightly modifies the shape of the Fermi surface, so that the nesting feature is survived with Weyl points in half-metallic \( \text{K}_2\text{Cr}_8\text{O}_{16} \). Besides the basic behavior of FM Weyl semimetal, it possesses several special features. Its non-trivial semimetal phase corresponds to a Peierls type metal–insulator transition. The coexistence of Weyl fermions and Fermi surface nesting is an unusual phenomenon due to the unique band structures in \( \text{K}_2\text{Cr}_8\text{O}_{16} \). This suggests that the metal–insulator transition of \( \text{K}_2\text{Cr}_8\text{O}_{16} \) starts from a topological non-trivial state. Such unusual accidental feature has never been reported in realistic materials previously. It is worth to mention that \( \text{K}_2\text{Cr}_8\text{O}_{16} \) hosts even pairs of Weyl points, which is in sharp contrast with that the FM Weyl semimetals usually possess odd pairs of Weyl fermions. In this work, we show that this exotic feature in \( \text{K}_2\text{Cr}_8\text{O}_{16} \) is protected by mirror reflection symmetry. In addition, the distribution of Weyl points in reciprocal space can be tuned by...
external magnetic fields, implying applications of topological control. All these phenomena deserve further attentions in future.

**Methods**

To investigate the electronic behavior of K$_2$Cr$_8$O$_{16}$, we perform first-principles calculations in the framework of density functional theory (DFT) [63, 64], as implemented in the Vienna _Ab initio_ Simulation Package [65]. The core-valence interactions are treated by the projector augmented wave method [66], where the plane wave expansion is truncated with a cutoff energy of 500 eV. We employ the exchange–correlation functional as the generalized gradient approximation (GGA) in the Perdew–Burke–Ernzerhof (PBE) formalism [67, 68]. For self-consistent calculations, a dense k-mesh with a $13 \times 13 \times 13$ Monkhorst–Pack grid [69] in momentum space is used to determine the band gap with spin–orbital-coupling (SOC). We introduce the on-site Coulomb repulsion, i.e. GGA + $U$ calculations [70] to describe the correlated effects of 3d electrons in Cr. The value of on-site Coulomb repulsion energy is chosen to be 3.0 eV [59], which works well in fitting the previous experimental data [54]. In addition, our additional results further show (see figure S1 stacks.iop.org/NJP/22/073062/mmedia) that in a wide range of $U$ (from 2.5 to 5.5 eV) the topological properties of K$_2$Cr$_8$O$_{16}$ are preserved near the Fermi level.

**Author contributions**

JZZ and YJJ contributed equally to this work. JZZ and YJJ conceived the original ideas. JZZ prepared the manuscript and performed part of the calculations. RW and BWX joined the discussions of the project and the improvement of the manuscript. HX supervised the project, joined the discussions of the whole project and the modification of the manuscript.

**Additional information**

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