# Chern Semimetal and the Quantized Anomalous Hall Effect in $HgCr_2Se_4$

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In 3D momentum space, a topological phase boundary separating the Chern insulating layers from normal insulating layers may exist, where the gap must be closed, resulting in a ''Chern semimetal'' state with topologically unavoidable band crossings at the Fermi level. This state is a condensed-matter realization of Weyl fermions in (3 + 1)D, and should exhibit remarkable features, such as magnetic monopoles and Fermi arcs. Here we predict, based on first principles calculations, that such a novel quantum state can be realized in a known ferromagnetic compound $HgCr_2Se_4$, with a single pair of Weyl fermions separated in momentum space. The quantum Hall effect without an external magnetic field can be achieved in its quantum-well structure.

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Under broken time reversal symmetry, the topological phases of two-dimensional (2D) insulators can be characterized by an integer invariant, called Chern number [1], which is also known as the TKNN number [2] or the number of chiral edge states [3] in the context of the quantum Hall effect. 2D insulators can thus be classified as normal insulators or Chern insulators depending on whether or not the Chern number vanishes. Since the Chern invariant is defined only for 2D insulators, it is natural to ask, what is its analog in 3D? Starting from a 2D Chern insulating plane (say at $k_z = 0$), and considering its evolution as a function of $k_z$, generally two situations may happen. If the dispersion along $k_z$ is weak, such that the Chern number remains unchanged, the system can be viewed as the simple stacking of 2D Chern insulating layers along the $z$ direction. Such 3D Chern insulators are trivial generalization of the Chern number to 3D, which is quite similar to the weak topological insulators in systems with time reversal symmetry. However, if the dispersion along $k_z$ is strong, such that Chern number changes as the function of $k_z$, the system will be in a nontrivial semimetal state with ''topologically unavoidable'' band crossings located at the phase boundary separating the insulating layers in $\vec{k}$ space with different Chern numbers [4,5]. This is due to the fact that the change of Chern number corresponds to a topological phase transition, which can happen only if the gap is closed. From the Kohn-Luttinger theorem, we can always expect that the band crossings appear at the Fermi level at stoichiometry.

This Chern semimetal state, if found to exist, can be regarded as a condensed-matter realization of (3 + 1)D chiral fermions (or called Weyl fermions) in the relativistic quantum field theory, where the field can be described by the 2-component Weyl spinors [6] (either left- or right-handed), which are half of the Dirac spinors and must appear in pairs. The band crossing points or Weyl nodes are topological objects in the following senses. First, since no mass is allowed in the $2 \times 2$ Hamiltonian, the Weyl nodes should be locally stable and can only be removed when a pair of Weyl nodes meet together in the $\vec{k}$ space. Second, the Weyl nodes are ''topological defects'' of the gauge field associated with the Berry's curvature in momentum space [7–9]. The gauge field around the neighborhood of the Weyl node must be singularly enhanced, and behaves like a magnetic field originating from a magnetic monopole [8]. The physical consequence of such a gauge field has been discussed in the context of the anomalous Hall effect [7,8,10] observed in ferromagnetic (FM) metals, where the Weyl nodes, if any, are always submerged by the complicated band structures.

In this Chern semimetal state, we may also expect unusual features like nonclosed Fermi surfaces (Fermi arcs) on the side surfaces. The possible Fermi arcs have been recently discussed from a view point of accidental degeneracy, and prospected for noncollinear antiferromagnetic pyrochlore iridates [11] by the fine-tuning of electron correlation $U$. Since the correct $U$ and the real magnetic ordering is still unknown, we have to wait for its material realization. In this Letter, we will show that such a novel Chern semimetal state is actually realized as the ground state of a known FM material $HgCr_2Se_4$, with only a single pair of Weyl nodes separated in the momentum space. We further find that the long-pursuing quantized anomalous Hall effect (QAHE) [12–15], i.e., the quantum Hall effect without an external magnetic field, can be achieved in the quantum-well structure of $HgCr_2Se_4$.

$HgCr_2Se_4$ is a FM spinel exhibiting large coupling effects between electronic and magnetic properties [16]. It shows novel properties like giant magnetoresistance [17], anomalous Hall effect [18], and the red shift of the optical absorption edge [19]. Its Curie temperature $T_c$ is high (around 106–120 K), and its saturated moment

 

is $5.64\mu_B$/f.u. [20,21], approaching the atomic value expected for high-spin $Cr^{3+}$. Its transport behavior is different from other FM chalcogenide spinels, like $CdCr_2Se_4$ and $CdCr_2S_4$, which are clearly semiconducting. $HgCr_2Se_4$ exhibits a semiconducting character in the paramagnetic state but a metallic state in the low temperature FM phase [17,22,23]. The spinel structure (space group $Fd\bar{3}m$) can be related to the zinc blende and diamond structures in the following way. If we treat the $Cr_2Se_4$ cluster as a single pseudoatom (called $X$) located at its mass center, then the Hg$X$ sublattice forms a zinc blende structure. There are two Hg$X$ sublattices in each unit cell, and they are connected by the inversion symmetry similar to the two atoms in the diamond structure. The pseudoatom $X$ is actually a small cube formed by Cr and Se atoms located at the cube corners. The cubes are connected by corner sharing the Cr atoms. As a result, each Cr atom is octahedrally coordinated by the 6 nearest Se atoms.

Our first principles calculations [24] confirm that the FM solution is considerably (2.8 eV/f.u.) more stable than the nonmagnetic solution, and the calculated moment ($6.0\mu_B$/f.u) is in good agreement with experiments [20,21]. The electronic structures shown in Figs. 1(a) and 1(b) suggest that the system can be approximately characterized as a "zero-gap half metal" in the case without spin-orbit coupling (SOC). It is almost a half metal because of the presence of a gap in the up-spin channel just above the Fermi level; it is nearly zero-gapped because of the band-touching around the Γ point just below the Fermi level in the down spin channel. The $3d$ states of $Cr^{3+}$ are strongly spin polarized, resulting in the configuration $t_{2g}^{3\uparrow} e_g^{0\uparrow} t_{2g}^{0\downarrow} e_g^{0\downarrow}$. The octahedral crystal field surrounding Cr atoms is strong and opens up a band gap between the $t_{2g}^{3\uparrow}$ and $e_g^{0\uparrow}$ manifolds. The Se-$4p$ states (located from about $-6$ to 0 eV) are almost fully occupied and contribute to the valence band top dominantly. Because of the hybridization with Cr-$3d$ states, the Se-$4p$ are slightly spin polarized but with an opposite moment (about $-0.08\mu_B$/Se). The zero-gap behavior in the down spin channel is the most important character here [Fig. 1(b)], because it suggests the inverted band structure around the Γ point, similar to the case of HgSe or HgTe [25,26].

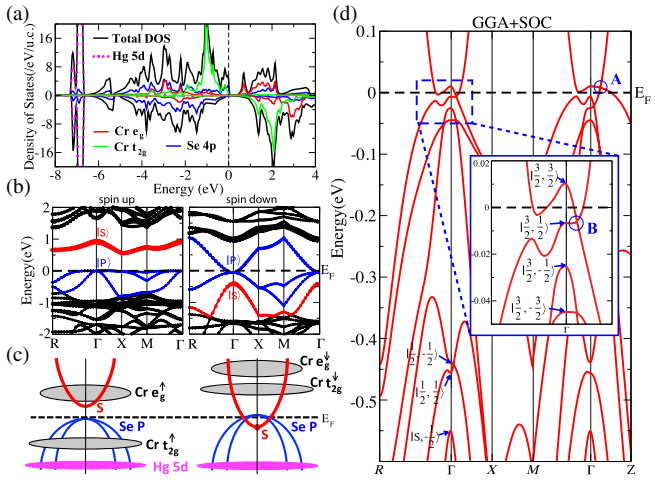


FIG. 1 (color online). Electronic structures of $HgCr_2Se_4$. (a) The total and partial density of states (DOS); (b) The band structures without SOC (showing the up and down spin parts separately); (c) The schematic understanding for the band inversion, where the $|S\rangle$ state is lower than the $|P\rangle$ states in the down spin channel; (d) The band structure after including SOC [with majority spin aligning to the (001) direction]. The low energy states at Γ are indicated as explained in the main text.

The four low energy states (8 after considering spin) at the Γ point can be identified as $|P_x\rangle$, $|P_y\rangle$, $|P_z\rangle$, and $|S\rangle$, which are linear combinations of atomic orbitals [27]. Considering these 4 states as bases, we now recover the same situation as HgSe or HgTe, and the only difference is the presence of exchange splitting in our case. Here the band inversion [see Fig. 1(c), $|S,\downarrow\rangle$ is lower than $|P,\downarrow\rangle$] is due to the following two factors. First, the Hg-$5d$ states are very shallow [located at about $-7.0$ eV, Fig. 1(a)] and its hybridization with Se-$4p$ states will push the antibonding Se-$4p$ states higher, similar to HgSe. In addition to that, the hybridization between unoccupied Cr-$3d^{\downarrow}$ and Hg-$6s^{\downarrow}$ states in the down spin channel will push the Hg-$6s^{\downarrow}$ state lower in energy [Figs. 1(b) and 1(c)]. As a result, the $|S,\downarrow\rangle$ is about 0.4 eV lower than the $|P,\downarrow\rangle$ states, and it is further enhanced to be 0.55 eV in the presence of SOC. We have to be aware of the correlation effect beyond the generalized gradient approximation (GGA), because the higher the Cr-$3d^{\downarrow}$ states, the weaker the hybridization with Hg-$6s^{\downarrow}$. It has been shown that semiconducting $CdCr_2S_4$ and $CdCr_2Se_4$ can be well described by the LDA + $U$ calculations with effective $U$ around 3.0 eV [28,29]. We have performed the same LDA + $U$ calculations for $HgCr_2Se_4$ and found that the band inversion remains unless the $U$ is unreasonably large ($> 8.0$ eV). The experimental observations of metallic behavior at low temperature for all kinds of samples [17,22,23] are strong supports to our conclusion for the inverted band structure.

In the presence of SOC, the new low energy eigenstates at Γ are given as $|\frac{3}{2},\pm\frac{3}{2}\rangle$, $|\frac{3}{2},\pm\frac{1}{2}\rangle$, $|\frac{1}{2},\pm\frac{1}{2}\rangle$, and $|S,\pm\frac{1}{2}\rangle$, which can be constructed from the $|P\rangle$ and $|S\rangle$ states [30], similar to HgSe again. Now, because of the exchange splitting in our case, the eight states at Γ are all energetically separated, with the $|\frac{3}{2},\frac{3}{2}\rangle$ having the highest energy, and the $|S,-\frac{1}{2}\rangle$ having the lowest. Because of the band inversion, several band crossings are observed, as shown in the band structure [Fig. 1(d)]. Among them, however, only two kinds of band crossings (called $A$ and $B$) are important for the states very close to the Fermi level. The crossing $A$ gives two points located at $k_z = \pm k_z^c$ along the $\Gamma - Z$ line, and the trajectory of crossing $B$ is a closed loop surrounding the Γ point in the $k_z = 0$ plane, as schematically shown in Fig. 2(a). For the 2D planes with fixed $k_z$ ($k_z \neq 0$ and $k_z \neq \pm k_z^c$), the band structures are all gapped (in the sense

that we can define a curved Fermi level). We can therefore evaluate its Chern number $C$ for each $k_z$-fixed plane. We found that $C = 0$ for the planes with $k_z < -k_z^c$ or $k_z > k_z^c$, while $C = 2$ for the planes with $-k_z^c < k_z < k_z^c$ and $k_z \neq 0$. We therefore conclude that the crossing $A$ located at the phase boundary between $C = 2$ and $C = 0$ planes (i.e, at $k_z = \pm k_z^c$) are topologically unavoidable Weyl nodes as addressed at the beginning. On the other hand, however, the crossing $B$ (i.e., the closed loop in $k_z = 0$ plane) is just accidental and it is due to the presence of crystal mirror symmetry with respect to the $k_z = 0$ plane. The crossing $B$ is not as stable as crossing $A$ in the sense that it can be eliminated by changing the crystal symmetry.

Using the 8 eigenstates at $\Gamma$, we can construct an $8 \times 8$ effective $\mathbf{k} \cdot \mathbf{p}$ Kane-Hamiltonian [30]. For qualitative understanding, however, we can downfold the $8 \times 8$ Hamiltonian into a simplest $2 \times 2$ model by considering the two bases $|\frac{3}{2}, \frac{3}{2}\rangle$ and $|S, -\frac{1}{2}\rangle$ which catch the band-inversion nature.

$$H_{\text{eff}} = \begin{bmatrix} M & Dk_z k_-^2 \\ Dk_z k_+^2 & -M \end{bmatrix}, \tag{1}$$

here $k_\pm = k_x \pm ik_y$, and $M = M_0 - \beta k^2$ is the mass term expanded to the second order, with parameters $M_0 > 0$ and $\beta > 0$ to ensure band inversion. Since the two bases have opposite parity, the off-diagonal element has to be odd in $k$. In addition, the $k_\pm^2$ has to appear to conserve the angular moment along the $z$ direction. Therefore, to the leading order, the $k_z k_\pm^2$ is the only possible form for the off-diagonal element. Evaluating the eigenvalues $E(k) = \pm\sqrt{M^2 + D^2 k_z^2 (k_x^2 + k_y^2)^2}$, we get two gapless solutions: one is the degenerate points along the $\Gamma - Z$ line with $k_z = \pm k_z^c = \pm\sqrt{M_0/\beta}$; the other is a circle around the $\Gamma$ point in the $k_z = 0$ plane determined from the equation $k_x^2 + k_y^2 = M_0/\beta$. They are exactly the band crossings obtained from our first-principles calculations. Because of the presence of $k_\pm^2$ in the off-diagonal element [31], it is easy to check that Chern number $C$ equals 2 for the planes with $-k_z^c < k_z < k_z^c$ and $k_z \neq 0$. The band dispersions near the Weyl nodes at the $k_z = \pm k_z^c$ plane [Fig. 2(c)] are thus quadratic rather than linear, with a chiral in-plane spin texture [shown in the inset of Fig. 2(c)]. The two Weyl nodes located at $\pm k_z^c$ have opposite chirality due to the opposite sign of the mass term, and they form a single pair of magnetic monopoles carrying the gauge flux in $\vec{k}$ space as shown in Fig. 2(d). The band crossing loop in the $k_z = 0$ plane is not topologically unavoidable; however, its existence requires that all gauge flux in the $k_z = 0$ plane (except the loop itself) must be zero.

This Chern semimetal state realized in $HgCr_2Se_4$ will lead to novel physical consequences, which can be measured experimentally. First, each $k_z$-fixed plane with a nonzero Chern number can be regarded as a 2D Chern insulator, and there must be chiral edge states for such plane if an edge is created. The number of edge states is two for the case of $C = 2$ [see Fig. 3(a)], or zero for the case of $C = 0$. If the chemical potential is located within the gap, only the chiral edge states can contribute to the Fermi surface, which are isolated points for each Chern insulating plane but nothing for the plane with $C = 0$. Therefore, the trajectory of such points in the $(k_x, k_z)$ surface or $(k_y, k_z)$ surface form nonclosed Fermi arcs, which can be measured by ARPES. As shown in Fig. 3(b), the Fermi arcs end at $k_z = \pm k_z^c$, and are interrupted by the $k_z = 0$ plane. This is very different from conventional metals, where the Fermi surfaces must be either closed or interrupted by the Brillouin zone boundary. The possible Fermi arcs have been recently discussed from a viewpoint of accidental degeneracy for pyrochlore iri-

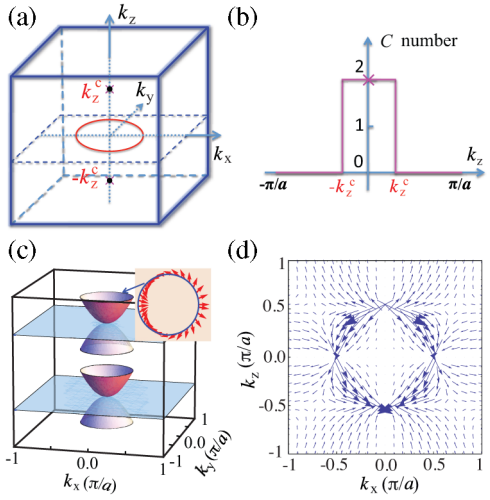


FIG. 2 (color online). Weyl nodes and gauge flux in $HgCr_2Se_4$ (a) The band crossing points in the $\vec{k}$ space; (b) The Chern number as function of $k_z$; (c) The schematic plot of the band dispersion around the Weyl nodes in the $k_z = \pm k_z^c$ plane, the inset shows the chiral spin texture; (d) The gauge flux evaluated as Berry curvature in the $(k_x, k_z)$ plane.

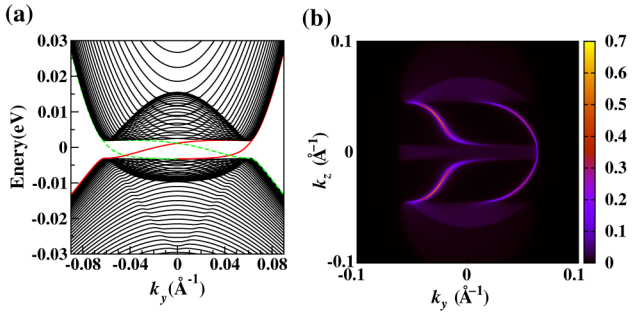


FIG. 3 (color online). Edge states and Fermi arcs of $HgCr_2Se_4$ [30]. (a) The edge states for the plane with $k_z = 0.06\pi$. A ribbon with two edges is used, and there are two edge states for each edge (because $C = 2$). The states located at different edges are indicated by different line types. (b) The calculated Fermi arcs for the $(k_y, k_z)$ side surface.

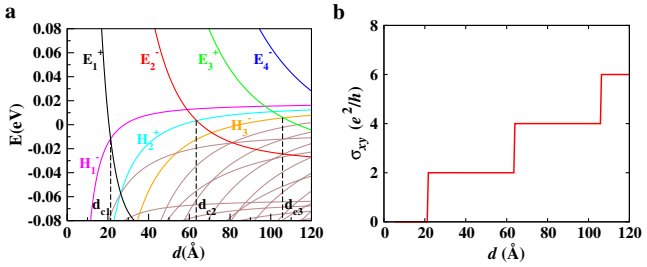


FIG. 4 (color online). Quantized anomalous Hall effect in $HgCr_2Se_4$ thin film [30]. (a) The subband energy levels at Γ point as a function of film thickness. (b) The Hall conductance as a function of film thickness.

dates [11]. Nevertheless, for the Chern semimetal state, the Fermi arcs should be more stable because the band crossings are topologically unavoidable.

The QAHE, on the other hand, is a unique physical consequence characterizing the Chern semimetal nature of $HgCr_2Se_4$, by considering its quantum-well structure. For 2D Chern insulators, the transverse Hall conductance should be quantized as $\sigma_{xy} = C\frac{e^2}{h}$, where $C$ is the Chern number. Such a quantum Hall effect without a magnetic field has been long pursued [12,13,15] but never achieved experimentally. In $HgCr_2Se_4$, considering the $k_z$-fixed planes, the Chern number $C$ is nonzero for limited regions of $k_z$, and this is due to the band inversion around Γ as discussed above. In the quantum-well structure, however, those low energy states around Γ should be further quantized into subbands (labeled as $|H_n\rangle$ and $|E_n\rangle$ for hole and electron subbands, respectively), whose energy levels change as a function of film thickness. As shown in Fig. 4(a), when the thickness of the film is thin enough, the band inversion in the bulk band structure will be removed entirely by the finite size effect. With the increment of the film thickness, finite size effect is getting weaker and the band inversion among these subbands restores subsequently, which leads to jumps in the Chern number or the Hall coefficient $\sigma_{xy}$ [14]. As shown in Fig. 4(b), if the film is thinner than 21 Å (about 2 lattice constants), the $\sigma_{xy}$ is zero; once the film thickness is larger than the critical thickness, we find subsequent jumps of $\sigma_{xy}$ in unit of $2e^2/h$. In fact, the strong anomalous Hall effect has been observed for the bulk samples of $HgCr_2Se_4$ [18]. This is in sharp contrast with pyrochlore iridates, where the anomalous Hall effect should be vanishing due to the AF ordering.

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first-principles calculations are given as $E_0 = 0.174$ eV, $\Delta_0 = 0.352$ eV, $P = 2.592$ eV Å, $m_s = 0.5424m_0$, and $m_p = -2.966m_0$. Two more parameters, describing the exchange splitting of electron and valence bands, are $h_s = 0.666$ eV and $h_p = 0.040$ eV. Replacing $k_x$ by $-i\hbar\partial_x$ and using the open boundary condition, we can diagonalize the Hamiltonian for each fixed $k_z$ and obtain the edge states. If we consider the open boundary condition along the $z$ direction, using the same strategy, we can evaluate the Hall conductance in the quantum-well structure. The QAHE is further confirmed by tight-binding calculations constructed from maximally localized Wannier functions.

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