Large-gap quantum anomalous Hall effect in monolayer halide perovskite

Zeyu Li,1 Yulei Han,2,1* and Zhenhua Qiao1,†

1ICQD, Hefei National Laboratory for Physical Sciences at Microscale, CAS Key Laboratory of Strongly-Coupled Quantum Matter Physics, and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China
2Department of Physics, Fuzhou University, Fuzhou, Fujian 350108, China

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We theoretically propose a family of structurally stable monolayer halide perovskite A$_2$B$_2$C$_9$ (A = Rb, Cs; B = Pd, Pt; C = Cl, Br) with easy magnetization planes. The family materials are all half metals with large spin gaps beyond 1 eV accompanying a single spin Dirac point located at K point. When the spin-orbit coupling is switched on, we further show that Rb$_3$Pt$_2$Cl$_9$, Cs$_3$Pd$_2$Cl$_9$, and Cs$_3$Pt$_2$Cl$_9$ monolayers can open up large band gaps from 63 to 103 meV to harbor quantum anomalous Hall effect with Chern numbers of $C = \pm 1$ whenever the mirror symmetry is broken by the in-plane magnetization, and the corresponding Berezinskii-Kosterlitz-Thouless transition temperatures are over 248 K. Our findings provide a potentially realizable platform to explore quantum anomalous Hall effect and spintronic applications at high temperatures.

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I. INTRODUCTION

Due to the topological protection from spatial separation, the Landau-level induced chiral edge modes make quantum Hall effect appealing in designing future low-power electronics [1]. In early time, the requirement of a strong magnetic field severely prevents the possible application of quantum Hall effect. Ever since the experimental discovery of graphene and topological insulators, various recipes were proposed to produce the quantum Hall effect without an external magnetic field, i.e., quantum anomalous Hall effect (QAHE). Two representative categories are monolayer atomic crystals (e.g., graphene and graphenelike materials) [2–4] and magnetic topological insulators [5–8]. On one side, in 2010 it was theoretically reported that graphene can open up a band gap to harbor QAHE in the presence of both Rashba spin-orbit coupling and magnetic field [9,10]. On the other side, it was still a challenge due to the weak Rashba spin-orbit coupling [9,10]. On the other side, nearly at the same time, a magnetic topological insulator was theoretically proposed to host QAHE via Cr dopants, and such a scheme was soon successfully realized in experiment at the extremely low temperature of 30 mK after three years’ efforts [11]. When more attention was focused on how to enhance the QAHE observation temperature, it was experimentally reported that the antiferromagnetic MnB$_2$Te$_4$ thin flakes can reach a record-breaking temperature of 6.5 K with the aid of an external magnetic field [12–15].

Nevertheless, the current achievement is still further away from the practical application. As an important material family, the perovskite ABO$_3$ consists of transition metal and heavy elements [16–20], implying a wonderland for breeding topological states, such as topological insulator, topological node-line semimetal, and topological crystalline metal [21–24]. Besides, several theoretical proposals have been suggested by building superlattices with a (111) bilayer rare-earth perovskite embedded inside wide-gap perovskites [25–28], where the major experimental difficulty is the requirement of precise alignment at the interfaces. Inspired by the broad interest of two-dimensional materials, the two-dimensional layered perovskites have also been experimentally prepared, e.g., 111-type In-based halide perovskite Cs$_3$In$_2$Cl$_9$ [29,30]. The layered perovskite materials display the possibility of realizing the QAHE due to their large intrinsic spin-orbit coupling and magnetism.

In this work, we theoretically predict a two-dimensional halide perovskite material family A$_3$B$_2$C$_9$, where A, B, and C represent alkali metal element (Rb, Cs), transition metal element (Pd, Pt), and halogen element (Cl, Br), respectively. They share the same structure as the monolayer Cs$_3$In$_2$Cl$_9$ with the transition metal atoms forming a buckled honeycomb lattice linked by halogen atoms. By performing first-principles calculations, we find that they are all half metals, with a huge spin splitting over 1.0 eV. The single spin Dirac point emerging at the K point is topologically protected by the trigonal crystal symmetry [31–33]. After the spin-orbit coupling is switched on, topologically nontrivial band gaps hosting QAHE open in monolayers Rb$_3$Pt$_2$Cl$_9$, Cs$_3$Pt$_2$Cl$_9$, and Cs$_3$Pd$_2$Cl$_9$, when the vertical mirror symmetry is broken by the magnetization. For the magnetization lying inside the plane, the nontrivial gaps can reach up to 103, 69, and 93 meV at the HSE06 level, greatly exceeding room temperature. Tuning the magnetization direction from in plane to out of plane will raise the gaps to 137, 99, and 100 meV, respectively. Monte Carlo calculations show that these three materials own a high Berezinskii-Kosterlitz-Thouless transition temperature above 248 K, implying the quasi-long-range order can be
observed at high temperatures like CoPS$_3$ [34]. The successful synthesis of Cs$_3$Fe$_2$Cl$_9$ [35] strongly indicates the possibility of realizing high temperature QAHE in our proposed monolayer halide perovskites.

II. CALCULATION METHODS

Our calculations were performed using the projected-augmented-wave method as implemented in the VASP package [36], and the generalized gradient approximation exchange-correlation [37] potential was used. The kinetic cutoff energy of the plane wave was set to be 500 eV. The Brillouin zone was sampled with a Γ-centered 13 × 13 × 1 grid based on the scheme proposed by Monkhorst and Pack for calculation of structural optimization and magnetic property, whereas a 6 × 6 × 1 grid was used for electronic structures [38]. A vacuum buffer space over 20 Å was included to prevent interaction between adjacent slabs. The convergence criterion was set to be $10^{-5}$ eV and $10^{-7}$ eV for energy in optimization and self-consistent field calculations, respectively. During structural optimization, all atoms were fully relaxed, and forces were converged to less than 0.0005 eV/Å. The phonon calculations were carried out by using the density functional perturbation theory as implemented in the Phonopy package with a $2 \times 2 \times 1$ supercell [39]. The screened hybrid functional (HSE06) method was applied to predict band gap closing to experiments [40]. The maximally localized Wannier functions were constructed by using the software package WANNIER90 with interfacing VASP [41,42]. The anomalous Hall conductivity was obtained by the interpolation of maximally localized Wannier functions. The anomalous Hall conductivity was obtained by summing Berry curvatures over all occupied valence bands:

$$\sigma_{\alpha\beta} = -\frac{e^2}{h} \int_{BZ} \frac{dk}{(2\pi)^2} \sum_n f_n(k) \Omega_{n\alpha\beta}(k).$$

The edge state was calculated by the iterative Green’s function method as implemented in the WANNIERTOOLS package [43]. Mcsolver code was used to perform Monte Carlo simulations on a $30 \times 30$ supercell with 200 000 steps at each temperature [44].

III. STRUCTURAL AND MAGNETIC PROPERTIES

Monolayer A$_3$B$_2$C$_9$ is crystallized in P-3m1 space group (No. 164), as depicted in Fig. 1(a). There are three vertical mirror planes across the high symmetry M point in the corresponding first Brillouin zone as shown in Fig. 1(b). Its primitive cell contains three alkaline metal atoms, two transition metal atoms, and nine halogen atoms. Each transition metal atom is surrounded by six nearest halogen atoms forming distorted octahedra. Monolayer A$_3$B$_2$C$_9$ exhibits five atomic layers, with transition metal atoms being located at different layers to form a buckled honeycomb lattice in favor of acquiring the Dirac point in electronic structure. The interaction between two transition metal atoms is bridged by a halogen atom forming the superexchange mechanism. Similar structure can be found in (111) bilayer transition metal oxide perovskite [27]. The alkali metal and halogen atoms at the outermost layers form a shield to protect the inner buckled honeycomb lattice composed of transition metal atoms from degradation of environment in monolayer A$_3$B$_2$C$_9$, leading to high stability of the structures as experimentally synthesized halide perovskites Cs$_3$In$_2$Cl$_9$ and Cs$_2$PtI$_6$ [30,45]. The structural stability of monolayer A$_3$B$_2$C$_9$ is also confirmed by phonon spectrum calculations [see Fig. 1(c) and Fig. 6]. The optimized lattice constants of monolayer A$_3$B$_2$C$_9$ (A = Rb, Cs; B = Pd, Pt; C = Cl, Br) are listed in Table I. Along with the increase of the atomic number of component elements, the lattice constants increase monotonically, ranging from 7.036 to 7.582 Å within the x-y plane and 5.763 to 6.252 Å along the z direction.

To determine the ground states of monolayer A$_3$B$_2$C$_9$, four representative magnetic configurations, i.e., ferromagnetic (FM), Néel antiferromagnetic (NAFM), stripe AFM (SAFM), and zigzag AFM (ZAFM), as shown in Fig. 2(a).

<p>| TABLE I. Lattice constants, magnetic ground state (GS), and exchange coupling constants of monolayer A$_3$B$_2$C$_9$. |
| --- | --- | --- | --- | --- |</p>
<table>
<thead>
<tr>
<th>A</th>
<th>C</th>
<th>GS</th>
<th>$J_1$ (meV)</th>
<th>$J_2$ (meV)</th>
<th>$J_3$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb$_2$Pd$_2$Cl$_6$</td>
<td>7.036</td>
<td>5.763</td>
<td>FM</td>
<td>−136.0</td>
<td>−1.7</td>
</tr>
<tr>
<td>Rb$_2$Pd$_2$Br$_6$</td>
<td>7.349</td>
<td>5.919</td>
<td>FM</td>
<td>−9.0</td>
<td>−2.0</td>
</tr>
<tr>
<td>Rb$_2$Pt$_2$Cl$_6$</td>
<td>7.061</td>
<td>5.756</td>
<td>FM</td>
<td>−123.6</td>
<td>−6.1</td>
</tr>
<tr>
<td>Rb$_2$Pt$_2$Br$_6$</td>
<td>7.385</td>
<td>5.898</td>
<td>FM</td>
<td>−20.5</td>
<td>−7.8</td>
</tr>
<tr>
<td>Cs$_3$Pd$_2$Cl$_6$</td>
<td>7.215</td>
<td>6.091</td>
<td>FM</td>
<td>−173.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Cs$_3$Pd$_2$Br$_6$</td>
<td>7.512</td>
<td>6.252</td>
<td>FM</td>
<td>−45.6</td>
<td>−4.1</td>
</tr>
<tr>
<td>Cs$_3$Pt$_2$Cl$_6$</td>
<td>7.209</td>
<td>6.098</td>
<td>FM</td>
<td>−115.8</td>
<td>−20.4</td>
</tr>
<tr>
<td>Cs$_3$Pt$_2$Br$_6$</td>
<td>7.582</td>
<td>6.203</td>
<td>FM</td>
<td>−59.2</td>
<td>−9.9</td>
</tr>
</tbody>
</table>
are considered. The GGA + U scheme is used to describe the on-site Coulomb repulsion on the d electrons of Pd and Pt atoms [46]. The value of U is set to be 3.5/2.5 eV for Pd/Pt, consistent with the result of the magnetic moment obtained from HSE06 calculation. The energies of different magnetic configurations are summarized in Table II, indicating that FM configuration is the most stable state for all monolayer A₂B₂C₉. The magnetic anisotropy energy (MAE) calculations show that the magnetization prefers to lie inside the x-y plane, such as Cs₃Pt₂Cl₉ shown in Fig. 2(b). The larger atomic number of occupation for each site leads to the enhanced MAE, e.g., the MAE in x-z plane increases from 62.2 μeV (Rb₃Pd₂Cl₉) to 2.6 μeV (Cs₃Pd₂Br₉). Although the Mermin-Wagner theorem prohibits long-range magnetic order in two-dimensional isotropic systems, a quasi-long-range order is allowed below the Berezinskii-Kosterlitz-Thouless critical temperature, such as VS₂ and FeCl₂ [47–49]. Based on the XY model, the Berezinskii-Kosterlitz-Thouless transition temperature is estimated up to the third neighbor coupling strength. The spin Hamiltonian is expressed as

\[ H = \sum_{\langle i,j \rangle} J_1 (S_i^x S_j^x + S_i^y S_j^y) + \sum_{\langle\langle i,j \rangle\rangle} J_2 (S_i^x S_j^y + S_i^y S_j^x) + \sum_{\langle\langle\langle i,j \rangle\rangle\rangle} J_3 (S_i^y S_j^x + S_i^x S_j^y), \]

where \( S^{x,y} \) is the spin operator and \( \langle \ldots \rangle, \langle \langle \ldots \rangle \rangle \), and \( \langle\langle\langle \ldots \rangle\rangle \rangle \) denote the sum over the nearest, the second, and the third neighboring sites. \( J_{1,2,3} \) denote the nearest, the second, and the third neighbor exchange interaction strengths, which can be extracted from the following equations:

\[ E_{\text{FM/NAFM}} = E_0 + (\pm 3J_1 + 6J_2 \pm 3J_3) \frac{S^2}{8}, \]

\[ E_{\text{SAFM/ZAFM}} = E_0 + (\mp J_1 - 2J_2 \pm 3J_3) \frac{S^2}{8}, \]

where \( E_0 \) is the ground state energy and \( S = 1/2 \) in our system.

IV. BAND STRUCTURES AND TOPOLOGICAL PROPERTIES

Now, let us move to the electronic properties of monolayer A₁₂B₂C₉. As depicted in Fig. 9, all A₁₂B₂C₉ monolayers are half metals with the Dirac point being located at the K point and the energy range with only one spin is over 1.0 eV, facilitating building spintronic devices with various materials. Along the high symmetry K-M line, the lowest unoccupied band crosses the Fermi level in five monolayer A₁₂B₂C₉, resulting in the absence of global gaps in the presence of spin-orbit coupling. After taking spin-orbit coupling into consideration, due to the lack of vertical mirror symmetry at K, a band gap opens regardless of the magnetization direction. Three Cl-based monolayers, i.e., Cs₃Pd₂Cl₉, Cs₃Pt₂Cl₉, and Rb₃Pt₂Cl₉, exhibit global band gaps. Herein below, we take the monolayer Cs₃Pt₂Cl₉ as an example of which the band structures are depicted in Fig. 3. In monolayer Cs₃Pt₂Cl₉, the Pt atom is in its +3 oxidation state with seven electrons filling the d orbitals. Because of the \( D_{3d} \) space group, the distorted octahedra around the Pt atom leads to the further splitting of d orbitals as shown in Fig. 5. Six electrons fill the lower d orbitals, whereas one electron fills a half of the \( (d_{xz}, d_{yz}) \) orbital making the system half metallic with pure spin polarization at the Fermi level. Furthermore, at the high symmetric point K, the Dirac point is protected by the group of wave vectors, i.e., the \( D_{3d} \) space group which owns a two-dimensional irreducible representation leading to the robust band crossing [Fig. 3(a)]. In the appearance of spin-orbit coupling, the band crossing is gapped by a Dirac mass term. The topological properties of the gap depend on the magnetization direction, i.e., (i) when the magnetization direction, e.g., along the x
FIG. 3. (a) Orbital projected (3d orbitals of Pt) band structure of monolayer Cs$_3$Pt$_2$Cl$_9$ without spin-orbit coupling where the $(d_{xz}, d_{yz})$ orbitals dominate the bands near the Fermi level. (b)–(d) Band structures with spin-orbit coupling when the magnetization direction is along $\phi = 0^\circ$, $45^\circ$ and $z$ direction, respectively.

axis, is perpendicular to the vertical mirror plane, the band gap would be trivial due to the symmetry restriction [50,51], and (ii) the remaining magnetization direction breaks the vertical mirror symmetry and induces a topologically nontrivial gap harboring QAHE. When the magnetization is along $\phi = 45^\circ$, as displayed in Fig. 3(c), a topologically nontrivial gap with Chern number of $C = 1$ can be produced. An out-of-plane magnetization further results in a larger topologically non-trivial gap up to 137 meV as shown in Fig. 3(d). Moreover, the QAHE is magnetization orientation dependent with alternating Chern numbers of $C = \pm 1$ [52]. As displayed in Fig. 4, the Chern number can be tuned from $+1(-1)$ to $-1(+1)$ by rotating the magnetization direction in the $x$-$y$ plane. Due to the negligible MAE in the $x$-$y$ plane, a tiny magnetic field can be used to rotate the in-plane magnetization direction and enhance the effective anisotropy as employed in the Cr$_2$Ge$_2$Te$_6$ film [53], indicating the feasibility of magnetization direction tunable topological phases in our proposed systems.

V. MATERIALS SYNTHESIS

As a big materials family, halide perovskite consists of a number of two-dimensional layered materials. Except for the 111-type In-based halide perovskite Cs$_3$In$_2$Cl$_9$, it was found that Cs$_3$Fe$_2$Cl$_9$ has been synthesized in 1954 [35]. This means that through proper modulation of synthesis, it is promising to produce the materials of monolayer A$_3$B$_2$C$_9$ for the study of high temperature QAHE.

VI. SUMMARY

We theoretically proposed a two-dimensional halide perovskite family A$_3$B$_2$C$_9$ (A = Rb, Cs; B = Pd, Pt; C = Cl, Br). We find that five of them are half metals with widely fully
spin-polarized energy range. When spin-orbit coupling is further considered, we show that monolayers Cs$_3$Pd$_2$Cl$_9$, Cs$_3$Pt$_2$Cl$_9$, and Rb$_3$Pt$_2$Cl$_9$ can open up topologically nontrivial band gaps of $\sim 100$ meV to realize high temperature QAHE with Chern numbers of $C = \pm 1$. A small external magnetic field can be applied to tune the sign of Chern number by altering the magnetization direction. Our proposed material systems of A$_3$B$_2$C$_9$ are experimentally feasible, because of the successful synthesis of Cs$_3$In$_2$Cl$_9$ and Cs$_3$Fe$_2$Cl$_9$ crystal. Our findings provide a platform for realizing high temperature QAHE in the intrinsic two-dimensional halide perovskite.

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APPENDIX A: LAYERED STRUCTURE AND DISTORTED OCTAHEDRA STRUCTURE IN MONOLAYER A$_3$B$_2$C$_9$

As shown in Fig. 5, monolayer A$_3$B$_2$C$_9$ (A = Rb, Cs; B = Pd, Pt; C = Cl, Br) comprise the five atomic layers where the transitional metal atoms are embedded in the second and fourth layer. The octahedra around transitional metal atoms is distorted at some extent. Taking Cs$_3$Pt$_2$Cl$_9$ as an example, one can find the internal and external bond length between transition metal atom and halogen atom are different. Usually, $d$ orbitals are split into $t_{2g}$ and $e_g$ groups in an octahedra crystal structure.
field. In monolayer $A_3B_2C_9$, the distorted octahedra crystal field will further split $t_{2g}$ group into $a_g$ and $e'_g$ required by $D_3^2$ space group, as shown in Fig. 5(c).

APPENDIX B: PHONON SPECTRUM OF MONOLAYER $A_3B_2C_9$

In Fig. 6, we plot the phonon spectrum of all monolayer $A_3B_2C_9$. The absence of imaginary frequency mode in monolayer $A_3B_2C_9$ indicates the stability of structures.

APPENDIX C: MAGNETIC PROPERTIES OF MONOLAYER $A_3B_2C_9$

In this part, we summarize the magnetic properties of monolayer $A_3B_2C_9$. Table II displays the total energy of all monolayer $A_3B_2C_9$ in the four magnetic configurations where the ferromagnetic and three kinds of antiferromagnetic states are considered. One can find that the ferromagnetic configuration is the ground state for all monolayer $A_3B_2C_9$.

Figure 7 displays the magnetic anisotropy energy (MAE) of monolayer $A_3B_2C_9$ ($A = \text{Rb, Cs}; B = \text{Pd, Pt}; C = \text{Cl, Br}$). The lower MAE within the $x$-$y$ plane indicates that the magnetization direction prefers to lie in the $x$-$y$ plane. Especially,
there is a tiny in-plane anisotropy (6 μeV) with a period of 60° in monolayer Rb$_3$Pd$_2$Br$_9$.

In Fig. 8, we plot the normalized magnetic moment of monolayers Rb$_3$Pd$_2$Cl$_9$, Rb$_3$Pd$_2$Br$_9$, Cs$_3$Pd$_2$Br$_9$, Rb$_3$Pt$_2$Br$_9$, and Cs$_3$Pt$_2$Br$_9$ as a function of temperature by Monte Carlo simulations. The critical temperatures of the Berezinskii-Kosterlitz-Thouless transition for monolayers Rb$_3$Pd$_2$Cl$_9$, Rb$_3$Pd$_2$Br$_9$, and Cs$_3$Pd$_2$Br$_9$ are 263, 47, and 127 K, respectively. For monolayers Rb$_3$Pt$_2$Br$_9$ and Cs$_3$Pt$_2$Br$_9$, the critical temperatures are 107 and 188 K, respectively.

**APPENDIX D: BAND STRUCTURE OF MONOLAYER A$_3$B$_2$C$_9$ WITHOUT AND WITH SPIN-ORBIT COUPLING**

As shown in Fig. 9, the band structures of all monolayer A$_3$B$_2$C$_9$ are depicted. In the absence of spin-orbit coupling, we can see that all A$_3$B$_2$C$_9$ monolayers are half metals with a Dirac point located at K point. The big energy windows with one spin channel (the gray area) range from 1.1 to 1.5 eV exhibiting great promise for the application of spintronic devices. After taking spin-orbit coupling into consideration, the nontrivial global gaps can be opened in monolayers Cs$_3$Pd$_2$Cl$_9$, Cs$_3$Pt$_2$Cl$_9$, and Rb$_3$Pt$_2$Cl$_9$ with Chern numbers of $C = \pm 1$ when the vertical mirror symmetry is broken.

**APPENDIX E: TOPOLOGICAL PROPERTIES OF MONOLAYERS RB$_3$PT$_2$CL$_9$ AND CS$_3$PD$_2$CL$_9$**

In Fig. 10, we plot the band structures and anomalous Hall conductivity of monolayers Rb$_3$Pt$_2$Cl$_9$ and Cs$_3$Pd$_2$Cl$_9$, respectively. After the spin-orbit coupling is switched on a global band gap of 69 meV opens in Rb$_3$Pt$_2$Cl$_9$ with in-plane magnetization. And the gap can be further increased to 99 meV with out-of-plane magnetization. Similarly, in monolayer Cs$_3$Pd$_2$Cl$_9$, the global band gap increases from 93 meV to 100 meV when the magnetization direction is tuned from in plane to out of plane. The topological properties can be examined by the quantized anomalous Hall conductivity as shown in Figs. 10(b) and 10(c) and Figs. 10(e) and 10(f).

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