Supplementary Information

Distinct ferrovalley characteristic for Janus RuClX (X = F, Br) monolayer

Yubiao Ma*a, Yanzhao Wu*a, Junwei Tongb, Li Denga, Xiang Yin*a, Lianqun Zhouc, Xiaoli Hand, Fubo Tieane, and Xianmin Zhang*a

*aKey Laboratory for Anisotropy and Texture of Materials (Ministry of Education), School of Material Science and Engineering, Northeastern University, Shenyang, 110819, China
*bDepartment of Physics, Freie Universität Berlin, Berlin, 14195, Germany
*cSuzhou Institute of Biomedical Engineering and Technology, Chinese Academy of Sciences, Suzhou 215163, China
*dTaian Weiye Electromechanical Technology Co., Ltd, Taian, 271000, China
*eState Key Laboratory of Superhard Materials, College of Physics, Jilin University, Changchun, 130012, China

Figures S1(a) and S1(b) show the spin charge density distribution of RuClF and RuClBr monolayers with FM and AFM states, respectively. It can be seen that the spin charge density of both spin-up (yellow in Figures S1) and spin-down (cyan in Figures S1) orientations is mainly concentrated on the Ru atoms, while the spin charge density of Cl, F or Br atoms are small enough to be neglected. This proves that the moment of RuClX monolayer is mainly contributed by the Ru atoms.

![Figure S1](image_url)

**Figure S1.** The spin charge density of the FM and AFM states for (a) RuClF and (b) RuClBr monolayers, respectively. The yellow and cyan represent spin up and spin down charge density, respectively. The isovalue is 0.04 e/Bohr³.

Figures S2(a) and (b) show the projected density of states of Ru-d, Cl-p and F/Br-p orbitals in RuClF and RuClBr monolayers. It is found that dxy and dx²-2y², dzy and dxz, px and py orbitals are degenerate. By comparing Figure S2(a) and Figure S2(b), it can be found that the strength of the unoccupied states (at the energy positive of 1 eV) d² orbitals is smaller in Figure S2(b). Thus, the interaction between the occupied spin-up states of dxz and the unoccupied spin-down states of d² orbitals in RuClBr monolayer would generate a smaller out-of-plane magnetic anisotropy.

![Figure S2](image_url)
**Figure S2.** (a) The projected density of states (PDOS) of Ru, Cl and F atoms in RuClF monolayer. (b) The PDOS of Ru, Cl and Br atoms in RuClBr monolayer. Fermi energy level is set to zero.

Figures S3(a)-S3(e) show the d-orbitals projected band structures of Ru atoms in the RuClF monolayer. As shown in Figures S3(a) and S3(e), the valley states at the K and K’ points are mainly contributed by the occupied $d_{xy}$ and $d_{x^2-y^2}$ orbitals of Ru atoms. The $d_{z^2}$ orbitals of Ru atoms are mainly distributed near the K and K’ points of the conduction band, as displayed in Figure S3(c).

**Figure S3.** (a)-(e) Projected band structures of Ru-d orbitals for the RuClF monolayer. Fermi energy level is set to zero.
Figure S4(a)-S4(e) show the d-orbitals projected band structures of Ru atom in the RuClBr monolayer. From Figures S4(a) and S4(e), it is found that the valley states at the K and K’ points are mainly contributed by the unoccupied d_{xy} and d_{x^2-y^2} orbitals of Ru atoms. As shown in Figure S4(c), the d_{z^2} orbitals of Ru atoms are mainly distributed near the K and K’ points of the valence band.

The 4d orbitals of Ru atom, the 2p orbitals of F atom, the 3p orbitals of Cl atom, and 4p orbitals of Br atom are considered as the projected orbitals in calculating Wannier functions for the present RuClF and RuClBr monolayers, respectively. The corresponding parameters of the frozen and outer energy windows for Wannier fitting are list in Table S1.

**Table S1.** The parameters of the frozen and outer energy windows for Wannier fitting.

<table>
<thead>
<tr>
<th>System</th>
<th>Frozen energy windows (eV)</th>
<th>Outer energy windows (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RuClF</td>
<td>-10.50, -1.98</td>
<td>-12.0, 2.0</td>
</tr>
<tr>
<td>RuClBr</td>
<td>-8.90, -1.0</td>
<td>-9.30, 8.0</td>
</tr>
</tbody>
</table>

Figure S5 presents the calculated data by the VASP method and the fitting results using
WANNIER functions for RuClF and RuClBr monolayers. It can be seen that the WANNIER fitted band structures are nearly identical with the VASP calculated results.

Figure S5. The calculated data by the VASP method and the fitting results using WANNIER functions for (a) RuClF and (b) RuClBr monolayers.

Figure S6 shows the final Wannier spread for each of wave function for RuClF monolayer. The Wannier spread for each of wave function is smaller than the lattice constant. The optimized lattice constant of RuClF monolayer is 3.34 Å.

Figure S6. The final Wannier spread for each of wave function for RuClF monolayer.

Figure S7 shows the final Wannier spread for each of wave function for RuClBr monolayer. The Wannier spread for each of wave function is smaller than the lattice constant. The optimized lattice constant of RuClBr monolayer is 3.66 Å.

Figure S7. The final Wannier spread for each of wave function for RuClBr monolayer.

As observed in Figure S8(a), with 0.05 holes per f.u. are doped, the Fermi energy level passes
through the $K'$ valley in RuClF monolayer. Therefore, the carriers are dominated by the $K'$ valley. The Fermi energy level passes through the $K$ valley in RuClBr monolayer with doping 0.05 electrons per f.u., as shown in Figure S8(b). At this time, the carriers are excited by the $K$ valley. In the first-principles calculations, carrier doping is simulated by removing or adding electrons from the system and using a homogeneous background charge to maintain charge neutrality\cite{1,2}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{s8.png}
\caption{(a) The band structures with SOC of RuClF monolayer with doping 0.05 holes per f.u. (b) The band structures with SOC of RuClBr monolayer with doping 0.05 electrons per f.u. The red arrow represents spin up, and the blue arrow represents spin down. Fermi energy level is set to zero.}
\end{figure}

References

\begin{enumerate}
\item X. Li, X. Wu, J. Yang, Half-Metallicity in MnPSe\textsubscript{3} Exfoliated Nanosheet with Carrier Doping, \textit{Journal of the American Chemical Society}, \textbf{136} 11065 (2014).
\end{enumerate}