Prediction of High Curie Temperature, Large Magnetic Crystal Anisotropy, and Carrier Doping-Induced Half-Metallicity in Two-Dimensional Ferromagnetic FeX$_3$ ($X = F$, Cl, Br, and I) Monolayers

Zhao Yong Guan* and Shuang Ni

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Two-dimensional (2D) intrinsic ferromagnetic (FM) semiconductors (SCs) are urgent for spintronics. FeX$_3$ ($X = F$, Cl, Br, and I) monolayers with intrinsic ferromagnetism are fabricated by density functional theory and confirmed by a global minimum search. FeX$_3$ ($X = F$, Cl, Br, and I) show a FM ground state, while an AFM-ZZ order has the second lowest energy. FeX$_3$ ($X = F$, Cl, Br, and I) have a Curie temperature ($T_c$) of 56, 716, 116, and 148 K, respectively. FeX$_3$ ($X = F$ and Cl) are bipolar magnetic semiconductors (BMSs), while FeX$_3$ ($X = Br$ and I) are half-semiconductors (HSCs). FeF$_3$ has a direct gap of 4.78 eV, while FeX$_3$ ($X = Cl$, Br, and I) have indirect band gaps of 2.92, 2.36, and 1.69 eV, respectively. They show perpendicular magnetic anisotropy, with a magnetic anisotropy energy (MAE) of 0.08, 0.11, 0.59, and 3.19 meV, respectively. All FeX$_3$ show good dynamical and thermal stability. Moreover, charge doping can transform FeCl$_3$, with an FM order to a half-metal (HM) with ferrimagnetic (Ferrim) or FM orders. However, FeI$_3$ could be transformed from the HSC into an HM with Ferrim or FM orders. The high $T_c$, large MAE, and tunable electromagnetic properties suggest that 2D FeX$_3$ ($X = F$, Cl, Br, and I) are promising magnetic SCs for potential application in electronics and spintronics.

1. INTRODUCTION

Since the discovery of graphene, a two-dimensional (2D) material has shown attractive properties and played an important role in modern electronics, spintronics, and magnetoelectronic devices. Graphene shows interesting physical and electronic properties. Other 2D materials, such as hexagonal boron nitride, transition-metal dichalcogenides, and stanene, have been found and presented attractive physical properties. Most 2D materials are non-magnetic. Because the long-range magnetic order at a finite temperature in 2D materials is forbidden, 2D ferromagnetic (FM) materials have not appeared until recent years, which limits 2D materials’ application in electronics and spintronics. 2D van der Waals materials with intrinsic ferromagnetism, such as CrI$_3$ (CrBr$_3$), Fe$_2$GeTe$_2$, Cr$_2$Ge$_2$Te$_6$, and 2H-VSe$_2$, have been successfully synthesized in the experiments. Cr$_2$Ge$_2$Te$_6$ and Fe$_2$GeTe$_2$ are FM materials with a $T_c$ of 220 and 223 K, respectively. However, Cr$_2$Ge$_2$Te$_6$ and Fe$_2$GeTe$_2$ are metals, which restricts their wide application (such as field effect transistors) in electronics. 2H-VSe$_2$ has a higher $T_c$ of 300 K with an intrinsic FM order, but its magnetic order is related to the substrate. In summary, magnetic semiconductors (SCs) are rare. Moreover, the $T_c$ of these FM materials is usually quite low. The ferromagnetism in SCs usually originates from d-p-d superexchange interaction. Therefore, it is quite weak, which hinders the wide application of 2D materials in spintronics.

Tunable FM orders, semiconductive properties, and high $T_c$ are expected in 2D magnetic materials. To increase $T_c$ and improve magnetic stability, researchers have tried to modulate, synthesize, and design various magnetic SCs. CrI$_3$ van der Waals structures have been successfully synthesized in the experiment, and magnetic orders are dependent on the layers and stacking patterns. However, the corresponding $T_c$ is much lower than room temperature. Therefore, many researchers have tried to increase $T_c$ and control the magnetic properties of CrI$_3$. 2D materials and CrI$_3$ could form all kinds of vdW structures, which show amazing electronic, magnetic, and valleytronics.
phase transition\(^{18}\) appears, and the corresponding \(T_c\) could be modulated (\(T_c^{\text{CrBr}_3} = 41.3\) K and \(T_c^{\text{CrCl}_3} = 29.7\) K).\(^{49}\) What are the properties of \(\text{ML}_3\) when \(\text{Cr}\) and \(I\) atoms in \(\text{CrI}_3\) are replaced by other transitional metals (\(\text{Fe}\)) and halogen atoms (\(\text{F}, \text{Cl}, \text{Br},\) and \(I\)) in the meantime?

In this article, we perform a systematic study on \(\text{FeX}_3\) (\(X = \text{F}, \text{Cl}, \text{Br},\) and \(I\)) monolayer (MLs), using density functional theory and a global minimum search. The intrinsic ferromagnetism in \(\text{FeX}_3\) originates from the superexchange interaction of \(\text{Fe}--\text{X}--\text{Fe}\) bonds. The energy difference of \(\text{FeX}_3\) (\(X = \text{F}, \text{Cl}, \text{Br},\) and \(I\)) between FM and AFM-ZZ orders is 0.011, 0.138, 0.023, and 0.029 eV, respectively. \(\text{FeX}_3\) (\(X = \text{F}\) and \(\text{Cl}\)) are bipolar magnetic semiconductors (BMSs), while \(\text{FeX}_3\) (\(X = \text{Br}\) and \(I\)) are half-semiconductors (HSCs). \(\text{FeF}_3\) has a direct gap, while other \(\text{FeX}_3\) have an indirect gap. The corresponding \(T_c\) is 56 (\(\text{FeF}_3\)), 716 (\(\text{FeCl}_3\)), 116 (\(\text{FeBr}_3\)), and 148 K (\(\text{FeI}_3\)), respectively. They all show perpendicular magnetic anisotropy (PMA) with large MAE. All \(\text{FeX}_3\) show good dynamical and thermal stability. Charge doping could modulate \(\text{FeCl}_3\) and \(\text{FeI}_3\) from the BMS and HSC with an FM order to a half-metal (HM) with FM or Ferrim orders by changing super and direct exchange interaction, respectively. Our results will provide a view to understand magnetic and electronic properties of \(\text{FeX}_3\) MLs, which is useful for the design of new nanoelectronic devices based on the FM SCs.

\section{RESULTS AND DISCUSSION}

\subsection{Geometry of \(\text{FeX}_3\) ML}

The geometry of \(\text{FeX}_3\) ML is fabricated and confirmed by PSO\(^{59}\) based on the crystal structure analysis, shown in Figure 1a–c. The lattice parameters are obtained from fitting the energy with different strains, shown in Figure 1d–g. The corresponding optimized lattice parameters for \(\text{FeX}_3\) (\(X = \text{F}, \text{Cl}, \text{Br},\) and \(I\)) are 5.308, 6.217, 6.607, and 7.179 Å (shown in Table 1), which are little larger than the corresponding \(\text{CrX}_3\) (\(\text{CrF}_3 = 5.200\) Å, \(\text{CrCl}_3 = 5.952\) Å, \(\text{CrBr}_3 = 6.310\) Å, and \(\text{CrI}_3 = 6.842\) Å).\(^{58}\) The corresponding \(\text{Fe}--\text{X}--\text{Fe}\) bond is 1.971, 2.412, 2.579, and 2.798 Å, which is little larger than that of \(\text{CrX}_3\) (\(X = \text{F}, \text{Cl}, \text{Br},\) and \(I\)) bond is 1.950, 2.336, 2.492, and 2.705 Å, respectively.\(^{58}\) As the atomic number increases, the halogen atomic radius also increases from 71 (\(\text{F}\)), 99 (\(\text{Cl}\)), to 114 (\(\text{Br}\)), and 133 pm (\(\text{I}\)), respectively. As a result, the corresponding...
lattice parameter increases. More details could be found in Table 1.

### 3.2. Magnetic Properties

The magnetic properties of FeX₃ are investigated, and the magnetic moment mainly localizes at Fe atoms. Each Fe atom contributes 4.0 μ_B magnetic moment, for all FeX₃ (X = F, Cl, Br, and I). There are eight Fe atoms in the 2 × 2 × 1 cell. There is 32.0 μ_B magnetic moment for the FM order in the supercell. There are four different AFM orders, including AFM-Neel (AFM-N), AFM- stripy (AFM-ST), AFM-zigzag (AFM-ZZ), and AFM-Neel- stripy (AFM-N-ST) orders investigated in this work. For the considered AFM orders, four Fe atoms contribute 16.0 μ_B, while the other four Fe atoms contribute −16.0 μ_B magnetic moment. Therefore, the total magnetic moment equals to 0 μ_B.

Each of the Fe atoms in FeF₃, FeCl₃, FeBr₃, and FeI₃ shows an FM ground state. The FeF₃ and FeCl₃ are BMSs. There are three important differences between the AFM orders (shown in Table 2). Other orders such as noncollinear AFM orders have also been considered, but their energies are higher than the FM orders. The noncollinear AFM order results in the Dzyaloshinskii–Moriya interaction. In a word, all FeX₃ (X = F, Cl, Br, and I) MLs are intrinsic FM materials.

Why does FeX₃ present a FM order? Each Fe atom is coordinated by six ligands-X in FeX₃, shown in Figure S1. The X–Fe–X bonding angle (93.7, 90.4, 90.1, and 90.3°) is close to 90° (shown in Table 1), which results in FM coupling according to the Goodenough–Kanamori–Anderson (GKA) rules of the superexchange theorem. However, there is AFM coupling, which originates from direct Fe–Fe exchange interaction. The ground state is determined by the competition between FM and AFM interaction, similar to the CrI₃ ML.\(^\text{39}\)

### 3.3. Electronic Structure

The electronic properties are systematically investigated in this part, and the band structure and density of the state are shown in Figure 2f–i. For FeF₃ and FeCl₃, the valence band maximum (VBM) is contributed by the spin-α electrons, while the conduction band minimum (CBM) is contributed by the spin-β electrons. Therefore, FeF₃ and FeCl₃ are BMSs. There are three important defined parameters: \(\Delta E_1\), \(\Delta E_2\), and \(\Delta E_3\) to describe BMSs following the routines.\(^\text{3,11}\) The value of \(\Delta E_1\), \(\Delta E_2\), and \(\Delta E_3\) is 4.78, 3.84, 0.77 eV and 2.92, 4.46, and 0.12 eV for FeF₃ and FeCl₃, respectively. More details could be found in Figure S2a,b, in the Supporting Information. However, the VBM and CBM are contributed by spin-β electrons of FeBr₃ and FeI₃, which

---

**Table 1. Calculated Lattice Constants \(a_0\), Total Energy \(E_i\), Bond Angles \(\theta_i\), (〈X–Fe–X〉), Axial Bond Angles \(\theta_i\) (〈X–Fe–X〉), \(\theta_i\) (〈X–Fe–X〉), and Bond Length \(l\) for the FM Order of FeX₃ (X = F, Cl, Br, I)**

<table>
<thead>
<tr>
<th>system</th>
<th>(a_0(\text{Å}))</th>
<th>(-E_\text{i}(\text{eV}))</th>
<th>(\theta_\text{i}(\text{deg}))</th>
<th>(\theta_\text{β}(\text{deg}))</th>
<th>(\theta_\text{α}(\text{deg}))</th>
<th>(\theta_\text{o}(\text{deg}))</th>
<th>(l(\text{Å}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF₃</td>
<td>5.308</td>
<td>300.99</td>
<td>102.1</td>
<td>167.5</td>
<td>93.7</td>
<td>77.9</td>
<td>1.971</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>6.217</td>
<td>234.87</td>
<td>96.0</td>
<td>171.7</td>
<td>90.4</td>
<td>84.0</td>
<td>2.412</td>
</tr>
<tr>
<td>FeBr₃</td>
<td>6.607</td>
<td>212.72</td>
<td>95.2</td>
<td>172.5</td>
<td>90.1</td>
<td>84.8</td>
<td>2.579</td>
</tr>
<tr>
<td>FeI₃</td>
<td>7.179</td>
<td>190.17</td>
<td>95.6</td>
<td>172.1</td>
<td>90.3</td>
<td>84.4</td>
<td>2.798</td>
</tr>
</tbody>
</table>

---

**Figure 2.** (a–e) Spin charge densities of (a) AFM-ST, (b) AFM-N, (c) FM, (d) AFM-N-ST, and (e) AFM-ZZ orders of FeF₃. The isovalue is 0.06 e/Å³. The red and blue colors represent spin-α and spin-β electrons, respectively. The spin-polarized band structure and density of the state are shown in Figure 2f–i. For FeF₃ and FeCl₃, the valence band maximum (VBM) is contributed by the spin-α electrons, while the conduction band minimum (CBM) is contributed by the spin-β electrons. Therefore, FeF₃ and FeCl₃ are BMSs. There are three important defined parameters: \(\Delta E_1\), \(\Delta E_2\), and \(\Delta E_3\) to describe BMSs following the routines.\(^\text{3,11}\) The value of \(\Delta E_1\), \(\Delta E_2\), and \(\Delta E_3\) is 4.78, 3.84, 0.77 eV and 2.92, 4.46, and 0.12 eV for FeF₃ and FeCl₃, respectively. More details could be found in Figure S2a,b, in the Supporting Information. However, the VBM and CBM are contributed by spin-β electrons of FeBr₃ and FeI₃, which...
and Curie Temperature Are Listed

Table 2. Energy Difference (meV) between AFM and FM Orders, Magnetic Moment of Fe Atoms (μᵣ), Exchange Parameter, and Curie Temperature Are Listed

<table>
<thead>
<tr>
<th>SYS</th>
<th>ΔE_AFM - ST</th>
<th>ΔE_AFM - N</th>
<th>ΔE_AFM - N - S</th>
<th>ΔE_AFM - ZZ</th>
<th>MM</th>
<th>J (meV)</th>
<th>Tₑ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF₃</td>
<td>36</td>
<td>47</td>
<td>34</td>
<td>11</td>
<td>4.35</td>
<td>1.38</td>
<td>56</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>177</td>
<td>223</td>
<td>178</td>
<td>138</td>
<td>4.10</td>
<td>17.25</td>
<td>716</td>
</tr>
<tr>
<td>FeBr₃</td>
<td>75</td>
<td>138</td>
<td>77</td>
<td>23</td>
<td>4.01</td>
<td>2.88</td>
<td>116</td>
</tr>
<tr>
<td>FeI₃</td>
<td>93</td>
<td>176</td>
<td>97</td>
<td>29</td>
<td>3.88</td>
<td>3.63</td>
<td>148</td>
</tr>
</tbody>
</table>

implies that they are HSCs. Moreover, both the VBM and CBM occupied by the spin-β electrons are located at the Γ point of the first Brillouin zone (BZ) of FeF₃. The VBM is located at the Γ point, while the CBM contributed by the spin-β electrons are located at the F point of the first BZ. Therefore, FeCl₃, FeBr₃, and FeI₃ MLs are SCs with indirect band gaps of 2.92, 2.36, and 1.68 eV calculated by the HSE06 functional, respectively, shown in Table 3.

Table 3. Calculated Electronic Property, Band Gap, MAE, and Easy Magnetization Axis Are Listed

<table>
<thead>
<tr>
<th>SYS</th>
<th>Sc</th>
<th>gap (eV)</th>
<th>direct/ indirect</th>
<th>MAE (meV/cell)</th>
<th>EA magnets</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeF₃</td>
<td>BMS</td>
<td>4.78</td>
<td>D</td>
<td>0.08</td>
<td>c, Ising</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>BMS</td>
<td>2.92</td>
<td>I</td>
<td>0.11</td>
<td>c, Ising</td>
</tr>
<tr>
<td>FeBr₃</td>
<td>HSC</td>
<td>2.36</td>
<td>I</td>
<td>0.59</td>
<td>c, Ising</td>
</tr>
<tr>
<td>FeI₃</td>
<td>HSC</td>
<td>1.69</td>
<td>I</td>
<td>3.19</td>
<td>c, Ising</td>
</tr>
</tbody>
</table>

*The MAE is calculated with SOC.*

As HSCs, the gaps of spin-α (Eₐ₋α) and spin-β (Eₐ₋β) channels are usually different from each other. The spin-α electrons’ gaps are 7.38, 6.13, and 4.78 eV, while the spin-β electrons’ gaps are 2.98, 2.36, and 1.69 eV, for FeCl₃, FeBr₃, and FeI₃, respectively. Hence, spin-β electrons are more easily excited from the VB to the CB, compared with spin-α electrons. The VBM is mainly composed of X’s pₓ and pᵧ atomic orbitals, shown in Figure 2 and Figure S3a–f. However, the CBM is mainly contributed by the Fe’s dₓ²−ᵧ² (FeF₃) and dₓ²−ᵧ² atomic orbitals (FeCl₃, FeBr₃, and FeI₃), shown in Figure 3a–d and Figure S4a,b, respectively. The charge density of the VBM and CBM also confirms this conclusion. Moreover, the states above the Fermi level are composed of dₓ²−ᵧ², dᵧ, dₓᵧ, dₓzy, and dₓ−ᵧ atomic orbitals of Fe atoms, shown in Figure 3a–d. For FeF₃, the states above the Fermi level are mainly contributed by dₓ²−ᵧ², dᵧ, dₓᵧ, and dₓ−ᵧ atomic orbitals of Fe atoms. However, the states above the Fermi level are contributed by dₓ²−ᵧ², dᵧ, dₓᵧ, dₓzy, and dₓ−ᵧ atomic orbitals of Fe atoms for other FeX₃. Different occupation of the d-orbital affects the different electronic properties of FeX₃ (X = F, Cl, Br, and I), which originates from different negativity of X atoms in FeX₃. The LDA functional also confirms above the conclusion, and the corresponding band structures of FeCl₃ and FeBr₃ MLs are shown in Figure S5a,b, respectively.

There are Fe atoms in FeX₃. Therefore, the effect of SOC on the electronic properties of FeX₃ is also considered. The corresponding band structures with SOC with EA along [001] and [100] are calculated, shown in Figure S7a–h. Both the VBM and CBM of FeF₃ are located at the K point. Therefore, FeF₃ is still a SC with a direct gap of 4.78 eV. For FeCl₃ and FeBr₃, the VBM and CBM are located at the Γ point, while the CBMs are located at the F point, shown in Figure S7c–h. Hence, they are SCs with indirect band gaps of 2.91, 2.17, and 1.30 eV, respectively. For the heavier element, such as Br and I, there is an obvious energy-splitting at the K point, shown in Figure S7e–h. More details could be found in the Supporting Information. However, there is a difference between band structures without SOC and with SOC, when the atomic mass increases.

3.4 Curie Temperature. The FM materials with high Curie temperature (Tₑ) are highly desirable. It is expected that Tₑ is large enough in the application. The classic Ising model is used to evaluate J and Tₑ. The magnetic configurations are shown in Figure 4a,b, and we assume the interactions nearest-neighbor only. The Hamiltonian can be written as:

\[
H = -J \sum_{<ij>} S_i \times S_j
\]
ϕ = −. However, S = +FeBr3, and FeI3, respectively. The corresponding FeBr3, and FeI3 orders, respectively. The exchange parameter is calculated with eq 4, and result. The 4.0 simulation with larger cells with more loops gives a similar hard axis, it needs energy.38 This energy named MAE is to overcome the MAE (MCA) are expected in spintronics. Materials with high MAE (MCA) are expected in spintronics.

\[
E_{FM} = E_0 - \left( \frac{1}{2} \times 8 \times 3 \right) |S|^2
\]  

(2)

\[
E_{AFM-ZZ} = E_0 - 8 \times \left( -\frac{1}{2}\times 1 + \frac{1}{2} \times 1 \times 2 \right) |S|^2
\]  

(3)

\[
J = \frac{E_{AFM-ZZ} - E_{FM}}{8|S|^2}
\]  

(4)

where \(E_{FM}\) and \(E_{AFM-ZZ}\) represent energies of FM and AFM-ZZ (\(E_{AFM-ZZ} < E_{FM}\)). The energies of FM and AFM (AFM-ZZ) orders could be evaluated with eqs 2 and 3, respectively. The exchange parameter is calculated with eq 4, and J is equal to 1.38, 17.25, 2.88, and 3.63 meV for FeX3 (X = F, Cl, Br, and I), shown in Table 2. The mean field theory usually overestimates \(T_c\). Therefore, we use classic Heisenberg model Monte Carlo (MC) simulation to evaluate \(T_c\) by calculating the magnetic moment as a function of temperature. This code is developed by Prof. Hongjun Xiang. As a benchmark, the \(T_c\) of CrI3 is developed to be 51 K with this method, which agrees well with the experimental value of 45 K.7 A larger 90 × 90 cell with 1.0 × 107 loops is used in the \(T_c\) calculation. The simulation with larger cells with more loops gives a similar result. The 4.0 \(\mu_B\) magnetic moment per Fe atom drops quickly, and the paramagnetic orders are achieved at a temperature of 80, 840, 160, and 200 K for FeF3, FeCl3, FeBr3, and FeI3, respectively. The corresponding \(T_c\) values are predicted to be 56, 716, 116, and 148 K, respectively. The \(T_c\) of FeX3 (X = F, Cl, Br, and I) is higher than that of CrCl3 (12.1 K65 and 29.7 K65), CrBr3 (23.1 K65 and 41.3 K65), and CrI3 (42.2 K65 and 46.4 K65).

3.5. Magnetocrystalline Anisotropy. For magnetic materials, when a magnetic moment is switched from EA to hard axis, it needs energy.38 This energy named MAE is to overcome the “barrier.”33 MCA is MAE per unit area. The FM materials with high MAE (MCA) are expected in spintronics.

For systems with high symmetry, the energy at certain direction \((\theta, \phi)\) follows the following equation:66

\[
\Delta E_0 = K_1 \cos^2 \theta + K_2 \cos^4 \theta + K_3 \cos 3\phi
\]  

(5)

where \(E\) represents energy in a certain direction \((\theta, \phi)\) with the polar angle \(\theta\) and azimuthal angle \(\phi\). \(E_0\) presents the global energy minimum. \(K_1, K_2,\) and \(K_3\) represent quadratic and quartic contribution to the MAE, respectively. The energy difference \(\Delta E_0\) is independent of the in-plane azimuthal angle \(\phi\), which implies \(K_1 = 0\). More details are shown in Figure 5a–d. This point could also be concluded from the symmetry (FeX3 has the D3d space group). Therefore, eq 5 is simplified into the equation:

\[
\Delta E_0 = K_1 \cos^2 \theta + K_2 \cos^4 \theta
\]  

(6)

\[
\Delta E_0 = E_0 - E_0
\]

\[
\Delta E_0 = E - E_0
\]

where \(E\) equals 0 eV, when \(\theta = 0\). However, \(E_0\) reaches the maximum, as \(\theta\) equals 0. It indicates that EA prefers to be PMA (along the [001] direction). The energy difference \(\Delta E_0\) changes as a function of polar angle \(\theta\), shown in Figure 5a–d. However, the \(\Delta E_0\) is related to \(U_{eff}\) as MAE originates from SOC. When the effect of SOC is described by the GGA + U method, the evaluated value is affected by \(U_{eff}\) and more details could be found in Figure S8 and S9a,b. We have tested MCA with different \(U_{eff}\) and found that MAE and MCA are affected by \(U_{eff}\). When \(U_{eff}\) equals to 5.5 eV, \(\Delta E_0\) (with meV unit) follows the equation: \(\Delta E_0 = 0.0821 \cos^2 \theta + 0.0002 \cos^4 \theta\) (FeF3) and \(\Delta E_0 = 0.115 \cos^2 \theta + 0.00015 \cos^4 \theta\) (FeCl3). The corresponding equations are shown as follows: \(\Delta E_0 = 0.6002 \cos^2 \theta - 0.0004 \cos^4 \theta\) (FeBr3) and \(\Delta E_0 = 2.680 \cos^2 \theta + 0.523 \cos^4 \theta\) (FeI3). Therefore, the MAE and MCA could be evaluated with the following formulas:

MAE = \(E_{[100]} - E_{[001]}\)  

(8)

MCA = \(E_{[100]} - E_{[001]}\) = MAE/S  

(9)

\[
S = a^2 \sin \frac{\pi}{3}
\]  

(10)

\[
E_{[100]} \text{ and } E_{[001]} \text{ represent total energies with the magnetic axis along } [100] \text{ and } [001] \text{ directions, respectively. } S \text{ is the area of the supercell. When MCA and MCA are negative, it indicates an in-plane preference for magnetization (IMA). In contrast, the positive MAE (MCA) means that it intends PMA. The MAE of 2D materials is larger than that of three-dimensional materials for reduced dimensionality. FeX3 are 2D materials, which is expected to have a sizable MCA. The MAE (MCA) of
FeX₃ (X = F, Cl, Br, and I) MLs is 0.08 (MCA = 0.005 erg/cm²), 0.11 (0.055 erg/cm²), 0.59 (0.252 erg/cm²), and 3.19 (1.145 erg/cm²) meV when the \( U_{eff} \) equals to 5.5 eV (shown in Table 3). The FeX₃ shows positive MAE, which means that FeX₃ is an Ising magnet, shown in Table 3. MAEs are larger than that of CrBr₃ (0.16 meV)⁴⁹,⁶⁸ and CrI₃ (0.80 meV).⁷,⁴⁹ These values are larger than those of the most known 2D magnets.⁶⁹,⁷⁰ Why FeX₃ prefer PMA? It originates from the indirect SOC between Fe and X atoms, and a similar phenomenon also appears in CrI₃.⁷¹ Moreover, the strength of the indirect SOC also enhances as the halogen atomic number increases.⁷¹ Therefore, the MAE (MCA) increases from F, Cl to Br, I atoms. Moreover, FeX₃ (X = F, Cl, Br, and I) are Ising magnets, shown in Table 3.

The work function of FeX₃ is also evaluated by calculating xy-averaged electrostatic potential. The corresponding work functions are 6.99 (FeF₃), 8.47 (FeCl₃), 7.42 (FeBr₃), and 6.28 eV (FeI₃), which implies that electrons need different energies to excite from the VBM to the vacuum energy level. The corresponding xy-averaged electrostatic potential is shown in Figure S10a−d.

3.6. Dynamical and Thermal Stability. The dynamical stability of FeX₃ is confirmed via phonon dispersion curves and phonon density of the states, which show no obvious imaginary phonon modes. The highest vibration frequency is 12.19 (X = F), 9.35 (Cl), 7.01 (Br), and 5.81 (I) THZ, which is lower than that of CrF₃ (17.99 THZ), CrCl₃ (10.94 THZ), CrBr₃ (9.05 THZ), and CrI₃ (7.32 THZ), shown in Figure S11a−h, Supporting Information. It can be found that the contribution mainly comes from X atoms for the low frequency (0 < \( \epsilon < 3.5 \) THZ), shown in Figure 6a−d. On the contrary, Fe atoms do

![Figure 5. MAE varies as a function of polar angle \( \theta \) and \( \phi \) for (a, e) FeF₃, (b, f) FeCl₃, (c, g) FeBr₃, and (d, h) FeI₃ ML. The MAE is calculated with the GGA + U method.](image1)

![Figure 6. (a−d) Phonon spectrum density of the state of (a) FeF₃, (b) FeCl₃, (c) FeBr₃, and (d) FeI₃ ML. The red, blue, green, purple, and dark wine red lines represent Fe, F, Cl, Br, and I atoms' projected phonon DOS, respectively. (e−h) AIMD of the evaluation of energy at the PBE + U level for 10 ps at 300 K. The blue, green, purple, and wine red lines represent total energies of (e) FeF₃, (f) FeCl₃, (g) FeBr₃ and (h) FeI₃, respectively, and 0.018 eV per atom, respectively. The snapshots of the geometries, shown in Figure S12a−d, also confirm the intact structures. No obvious structure distortion is found, and FeX₃ is expected to be stabilized at room temperature. It is sure that the geometries of FeX₃ are stable at room temperature.](image2)
atoms (atomic weight: 52) are little lighter than Fe atoms (atomic weight: 55.85).

The thermal stability of FeX₃ is evaluated with AIMD, which is widely used to research the stability of materials. To examine whether FeX₃ is stable, we perform AIMD simulations at 300 K. The fluctuations in the total energies are shown in Figure 6e-h. The total energies of FeX₃ (X = F, Cl, Br, and I) vibrate around −172.96 eV (X = F), −122.09 eV (Cl), −109.00 eV (Br), and −95.26 eV (I) at 300 K, with the amplitude about 0.013, 0.011, and 0.015.

3.7. Carriers Modulate FeX₃ (X = Cl and I). In general, these synthesized 2D MLs are usually positively or negatively charged. Moreover, carrier doping is a common method to effectively control the magnetic and electronic properties of 2D materials. Therefore, it is necessary to explore the carrier’s doping effect on the properties of the FeX₃ ML. The VBM and CBM of BMS materials are contributed by different spin electrons. A little injected electrons (or holes) would only occupy the conduction band in one channel (or the valence band in another channel). Therefore, charge doping could drive a BMS-to-HM electronic phase transition. Moreover, HM can provide 100% spin-polarized carriers, which has wide applications in electronics. Previous studies have shown that it is likely to induce magnetic transition by carrier doping. The carrier doping could introduce unpaired p or d electrons. As a result, carrier doping is expected to manipulate the electromagnetic properties of the FeX₃ ML.

The charge doping could introduce magnetic phase transformation between FM and Ferrim orders in FeX₃. The carrier doping affects magnetic moments by introducing additional electrons or holes into the supercell. Taking FeCl₃ with a 2 × 2 × 1 cell as an example, it has 40 µB magnetic moment, and corresponding results are shown in Figure 7a. It is interesting that doping either n electrons or holes will reduce the magnetic moment with n µB, as ln < 0.39 e. ΔE is defined as the following equation: ΔE = E_FM − E_Ferrim - ZZ which is used to describe the energy difference between FM and Ferrim orders. The E_Ferrim - ZZ presents the total energy of the ferrimagnetic-zigzag (Ferrim-ZZ) order, which is similar to the AFM-ZZ order, shown in the inset of Figure 7a. When the negative carriers are further introduced, the direct exchange interaction between Fe atoms is further weakened. As the negatively doped charge is −0.39 e, the corresponding ΔE is −0.003 eV. Hence, there is a magnetic order transformation from FM to Ferrim orders at a critical carrier doping of −0.39 e. The FeCl₃ ML has ln µB magnetic moment. As more negative charges are further doped, ΔE are decreased to −0.221 eV (−0.6 e) and −0.327 eV (−0.9 e), respectively.

When the positive carriers are doped, the ΔE is first increased to 0.138 (+0.1 e), 0.139 (+0.2 e), 0.140 (+0.3 e), and 0.141 (+0.4 e) eV, respectively. When the q is large than 0.45 e, ΔE is monotonously decreased to 0.127 (+0.6 e), 0.069 (+0.9 e), and 0.032 eV (+1.2 e), respectively. As more positive carriers are doped, the ΔE decreases as the positive charge could suppress the super exchange interaction between Fe and Cl atoms. However, the ΔE is positive, which implies that FeCl₃ still shows a robust FM ordered ground state over a wide range.

The electronic properties are closely related to the magnetic orders, shown in Figure 7b-g and Figure S13a-h. The FeCl₃ ML represents a BMS without charge doping. When the negative carrier is doped with −0.2 e, the original VBM is contributed by spin-β electrons, while the CBM is contributed by the d (d_xy, d_yz, d_xz) orbital of spin-β electrons, shown in Figure 7d. Therefore, the FeCl₃ is still a BMS. As −0.6 e electrons are introduced, the spin-α electrons would partially occupy d_xy and d_xz, shown in Figure 7c. The FeCl₃ is transformed into a HM. In a word, the negative carriers would modulate FeCl₃ from the BMS with FM orders to BMS (FM or Ferrim orders) (lq < 0.39 e) or HM (Ferrim or FM orders) (lq > 0.39 e), shown in Figure S13a-d. When the positive charge is introduced, it means that part of electrons will be “pumped” from the VBM of FeCl₃. The states at the Fermi level are mainly contributed by spin-α electrons’ pₓ and pᵧ orbitals, shown in Figure 7e-g. When the less hole (q < 0.45 e) is introduced, FeCl₃ is still a BMS with an FM order, shown in Figure 7e and Figure S13e-h.

As more holes are doped, the states at the Fermi level also increase, shown in Figure 7f and Figure S13g.h. The spin-α electrons intend to partially occupy the Fermi level, while the spin-β electron channel shows insulating properties. Therefore, the positively charged (q > 0.45 e) FeCl₃ is transformed into a HM, whose spin-α electron is insulating, shown in Figure
S13g.h. In a word, the carrier could modulate magnetic and electronic properties by changing the super exchange interaction between Fe and Cl atoms or direct exchange interaction between Fe atoms, shown in Figure 7a. As a result, the FeCl$_3$ could be tuned from the BMS (FM order) to BMS (FM or Ferrim orders) or HM (FM or Ferrim orders), depending on the charge magnitude. More details could be found in Figure S13ah, in the Supporting Information. As FeI$_3$ is doped with the carriers, the corresponding magnetic moment and $\Delta E$ also change with the charge, shown in Figure 8a. The original FeI$_3$ is a HSC with an intrinsic FM order. In the previous work, the HSC could be easily tuned from the BMS (FM order) into HM with charge $q$. The corresponding net $\Delta E$ converted from FM to Ferrim orders (the corresponding net $\Delta E$ converted from FM to Ferrim orders) by carrier doping in a wide range. Our work found intrinsic ferromagnetism in FeX$_3$ MLs using particle-swarm search approaches and first-principles. All FeX$_3$ show an intrinsic FM order, and the ferromagnetism comes from the superexchange interaction of Fe–X–Fe bonds with angle close to 90°. FeX$_3$ (X = F, Cl, Br, and I) have a $T_{c}$ of 56, 716, 116, and 148 K, respectively. FeF$_3$ and FeCl$_3$ are BMSs with (direct) and (indirect) gaps of 4.78 and 2.92 eV, respectively, while FeBr$_3$ and FeI$_3$ are HSCs with indirect gaps of 2.36 and 1.69 eV, respectively. The EA of FeX$_3$ (X = F, Cl, Br, and I) is along the [001] direction, and MAE is 0.08, 0.11, 0.59, and 3.19 meV, respectively. The magnetic and electronic properties of FeX$_3$ (X = F, Cl, Br, and I) are different, which is attributed to the different Fe d-orbitals’ occupation. All FeX$_3$ show good dynamical and thermal stability. The FeCl$_3$ and FeI$_3$ can be transformed from the BMS or HSC (FM order) into HM (FM or Ferrim orders) by carrier doping in a wide range. Our work presents FM FeX$_3$ MLs with high Curie temperature, high MAE, and tunable electronic properties, implying wide potential application in spin-electronics.

4. CONCLUSIONS

In summary, we have predicted and investigated magnetic and electronic properties of FeX$_3$ (X = F, Cl, Br, and I) MLs. We have found intrinsic ferromagnetism in FeX$_3$ MLs using particle-swarm search approaches and first-principles. All FeX$_3$ show an intrinsic FM order, and the ferromagnetism comes from the superexchange interaction of Fe–X–Fe bonds with angle close to 90°. FeX$_3$ (X = F, Cl, Br, and I) have a $T_{c}$ of 56, 716, 116, and 148 K, respectively. FeF$_3$ and FeCl$_3$ are BMSs with (direct) and (indirect) gaps of 4.78 and 2.92 eV, respectively, while FeBr$_3$ and FeI$_3$ are HSCs with indirect gaps of 2.36 and 1.69 eV, respectively. The EA of FeX$_3$ (X = F, Cl, Br, and I) is along the [001] direction, and MAE is 0.08, 0.11, 0.59, and 3.19 meV, respectively. The magnetic and electronic properties of FeX$_3$ (X = F, Cl, Br, and I) are different, which is attributed to the different Fe d-orbitals’ occupation. All FeX$_3$ show good dynamical and thermal stability. The FeCl$_3$ and FeI$_3$ can be transformed from the BMS or HSC (FM order) into HM (FM or Ferrim orders) by carrier doping in a wide range. Our work presents FM FeX$_3$ MLs with high Curie temperature, high MAE, and tunable electronic properties, implying wide potential application in spin-electronics.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03915.

Information on materials, parameters in CALYPSO, band structure of FeF$_3$ and FeCl$_3$, p-orbital projected band structure of FeF$_3$ and FeCl$_3$, PDOS of FeF$_3$ and FeI$_3$, band structure with LDA, band structure with AFM orders, band structure with SOC, U test, MAE test, indirect SOC, work function, phonon spectrum and phonon density of ML CrX$_3$ (X = F, Cl, Br, and I), snapshots of the atomic structure with AIMD, and band structure of FeCl$_3$ doped with carriers (PDF)
The authors thank Prof. Wenhui Duan and Xingxing Li for financial support from the Natural Science Foundation of China; Shandong University, Jinan, Shandong 250100, P. R. China. The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Prof. Wenhui Duan and Xingxing Li for discussion of Curie temperature, Prof. Liang Ma, Shuqing Zhang, and Chunmei Zhang for calculation of MAE/energy, Discussion of evaluation of Curie temperature, Prof. Liang Ma, The authors thank Prof. Wenhui Duan and Xingxing Li for financial support from the Natural Science Foundation of China; Shandong University, Jinan, Shandong 250100, P. R. China. The authors declare no competing financial interest.

REFERENCES

Antiferromagnet-to-Ferromagnet Reversible Nonequilibrium Phase Transition within Van Der Waals Heterostructures: Current-Driven Direct Photoluminescence Probing of Ferromagnetism in Monolayer CrI3. DOI: 10.1103/PhysRevB.98.144411.

The Journal of Physical Chemistry C pubs.acs.org/JPCC

The Journal of Physical Chemistry C

Chem. C

DOI: 10.1103/PhysRevB.98.144411

2019

Chem. C

pubs.acs.org/JPCC

and Magnetic Crystal Anisotropy.

2D Materials

Ferromagnetic Janus VSeTe Monolayer. No. eaaw1874.

Stroppa, A. Magneto-Optical Kerr Switching Properties of (CrI3)2 and (CrBr3/CrI3) Bilayers. No. aac9439.

Dimensional Magnet CrI3. Approximation Made Simple. Via Particle-Swarm Optimization.

Boosting the Curie Temperature of Two-Dimensional Semiconductors with Transverse Electric Fields: First-Principles Calculations. For Metals and Semiconductors Using a Plane-Wave Basis Set. Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set.


Metal-Atom Adsorption onto Graphene Embedded with the Hexagonal Antiferromagnets. Reorientation Transitions, and Domain Structures in Planar Doping.


