**Two-Dimensional Half-Metallic and Semiconducting Lanthanide-Based MXenes**

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**ABSTRACT:** As a large family of two-dimensional materials, MXenes have attracted intensive attention in recent years. For more functional applications, it is of great significance to determine new MXene members. Here, we theoretically expand the M elements of MXenes to the lanthanide series. Based on density functional theory calculations, the bare lanthanide-based carbidic $\text{M}_2\text{C}$ ($\text{M} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$) and the corresponding fluorine- and hydroxyl-terminated configurations are investigated. Most of the fluorine- and hydroxyl-terminated MXenes investigated are half-metals. Specifically, in the half-metallic $\text{Eu}_2\text{C(OH)}_2$, the spin-down states show a band gap larger than 2 eV, implying this configuration’s potential applications in spin generation and injection. Both $\text{Gd}_2\text{CT}_2$ ($\text{T} = \text{F}$ and $\text{OH}$) are magnetic semiconductors. The former shows an indirect band gap of 1.38 eV, while the latter presents a direct one of 0.882 eV. These two configurations also show large magnetic moments higher than 13.7 $\mu_B$ per unit cell. All the hydroxyl-terminated MXene members show relatively low work functions, with the lowest value of 1.46 eV determined in Tm$_2$C(OH)$_2$. These predicted electronic properties imply that the lanthanide-based MXenes could have potential applications in spintronics, information storage, near-infrared detectors, field effect transistors, and field emitter cathodes.

**INTRODUCTION**

With the enhanced degree of integration, conventional silicon-based electronics encounter increasing challenges. For instance, the behavior of the circuit with the chip size at the nanoscale becomes unstable due to the quantum tunneling effect. Moreover, the performance of silicon transistors degrades at high temperatures because of the small band gap and unsatisfactory thermal conductivity. Regarding the development of next-generation electronics, to find promising elements of MXenes to the lanthanide series. Based on density functional theory calculations, the bare lanthanide-based carbidic $\text{M}_2\text{C}$ ($\text{M} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$) and the corresponding fluorine- and hydroxyl-terminated configurations are investigated. Most of the fluorine- and hydroxyl-terminated MXenes investigated are half-metals. Specifically, in the half-metallic $\text{Eu}_2\text{C(OH)}_2$, the spin-down states show a band gap larger than 2 eV, implying this configuration’s potential applications in spin generation and injection. Both $\text{Gd}_2\text{CT}_2$ ($\text{T} = \text{F}$ and $\text{OH}$) are magnetic semiconductors. The former shows an indirect band gap of 1.38 eV, while the latter presents a direct one of 0.882 eV. These two configurations also show large magnetic moments higher than 13.7 $\mu_B$ per unit cell. All the hydroxyl-terminated MXene members show relatively low work functions, with the lowest value of 1.46 eV determined in Tm$_2$C(OH)$_2$. These predicted electronic properties imply that the lanthanide-based MXenes could have potential applications in spintronics, information storage, near-infrared detectors, field effect transistors, and field emitter cathodes.

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lysts. Among these 2D carbides, most configurations are metallic. Only Mo$_2$CT, Mo$_2$TiC$_2$T$_5$ present semiconducting-like behaviors in experiments, with T$_5$ denoting surface functional group. Theoretically, several MXene members were determined to be semiconducting, such as M$_2$CO$_2$ (M = Sc, Ti, Zr, Hf, Mn and W), M$_2$C$_2$T$_5$ (Sc, Cr and Mo) and Sc$_4$C(OH)$_2$. Mn$_2$CF$_2$ was found to be a half-metal with a high Curie temperature of 520 K. M$_2$C and M$_2$N (M = Ti and V) were also predicted to show half-metallic or spin gapless semiconducting feature under strains. Obviously, it is feasible to tune the electronic properties of MXenes by varying their transition metals and surface groups.

Specially, MXenes with their transition metal in group IIIB generally show semiconducting characteristics regardless of functional groups, such as M$_2$CT$_2$ (M = Sc, Y, La and Lu; T = O, F and OH). M$_2$C(OH)$_2$ (M = Sc, Y and La) are the only three direct-band-gap semiconducting MXene members up to date. Sc$_2$CO$_2$ presents large out-of-plane polarization, which could have potential applications in piezoelectric and ferroelectric materials. Both Sc$_2$CT$_2$ (T = F and OH) and Lu$_2$CT$_2$ (T = F and OH) could be used in high-frequency semiconductor devices on the basis of their promising electron mobilities, where the electron mobility of Lu$_2$C(OH)$_2$ is nearly 10 times that of silicon. Moreover, the intermediate states Sc$_2$C(OH)$_2$O$_{2-x}$ among the transition from Sc$_2$C(OH)$_2$ to Sc$_2$CO$_2$ show magnetic semiconducting properties.

Based on the excellent semiconducting and spintronic properties reported for the MXenes with group IIIB transition metals, here we expand the M element of MXene to the lanthanide series. Based on the first-principles calculations, 12 bare M$_2$C MXenes (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) are first studied. The left lanthanide-based M$_2$C (M = La and Lu) have been reported previously. All of the structures investigated are found to be stabilized in the T-type configuration. Further, the structures, stabilities and electronic properties of corresponding fluorine- and hydroxyl-functionalized members are discussed. Most functionalized configurations are also predicted to be stable. The fluorine- and hydroxyl-functionalized structures are generally half-metallic except for M$_2$CT$_2$ (M = Ce, Tm, Gd and Yb). M$_2$CT$_2$ (M = Ce, Tm and Yb; T = F and OH) are magnetic metals. Gd$_2$CT$_2$ (T = F and OH) are magnetic semiconductors with their band gaps are 1.38 and 0.882 eV, respectively. Moreover, the hydroxyl-terminated MXenes generally show relatively low work functions.

### COMPUTATIONAL DETAILS

All the first-principles calculations are carried out using the Vienna Ab initio Simulation Package (VASP) code. The Perdew–Burke–Ernzerhof (PBE) scheme of generalized gradient approximation (GGA) is adopted for the exchange–correlation functional. A plane-wave cutoff energy of 500 eV based on the projector augmented-wave pseudopotential is utilized for describing the ion–electron interactions. All the structures are relaxed until the forces on each atom are less than 1.0 × 10$^{-4}$ eV/Å, and the energy tolerance is set as 1.0 × 10$^{-6}$ eV/unit cell. A Γ-centered 12 × 12 × 1 k-point mesh sampled in the hexagonal Brillouin zone (BZ) is adopted for structural optimization, and a 60 k-point grid along the high-symmetry routes of BZ is employed for plotting the electronic energy band. To eliminate the interactions of neighboring layers, a vacuum layer with its thickness larger than 15 Å is adopted. The layer thickness of MXene is chosen as the monomer thickness in its corresponding multilayer configuration, as reported in our previous work. To test the dynamic stability of MXenes, 4 × 4 × 1 supercells are considered for the phonon calculations from the density functional perturbation theory (DFPT) combined with the Phonopy and VASP software. The work function is calculated as the difference between the vacuum level and Fermi level of each configuration, and the vacuum level is obtained by plotting the average potential along the z-axis perpendicular to the MXene surface. All the calculations are based on the spin-polarization scheme. All the structures are visualized in the VESTA code.

In order to test the thermodynamic stability of the functionalized configurations, the formation energy is calculated according to the following equation:

$$\Delta E = E_{\text{tot}}(M_2CT_2) - E_{\text{tot}}(M_2C) - E_{\text{tot}}(T_2)$$

where $E_{\text{tot}}(M_2CT_2)$ denotes the total energy of the functionalized MXene, $E_{\text{tot}}(M_2C)$ is the total energy of bare MXene, and $E_{\text{tot}}(T_2)$ is the total energy of F$_2$ or O$_2$ + H$_2$ as the fluorine and hydroxyl groups are studied in our work.

### RESULTS AND DISCUSSION

In order to investigate the lanthanide-based MXenes, their structures and stabilities are first studied. The 2D bare transition-metal carbides could be categorized as T- and H-types, and both types of structures are shown in Figure 1. For the T-type configuration shown in Figure 1a, both the top and bottom transition metals are located in the triangle centers of neighboring carbon atoms. Many reported MXenes appeared in this type, for the H-type structure, the transition-metal atoms in the top layer are located on the top sites of the bottom transition metals. The well-known MoS$_2$ is stabilized in the H-type configuration.

Based on the unit cells, the relative total energies between the T- and H-type M$_2$C (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) are provided in Table S1 in Supporting Information. From the table, it is observed that the T-type configurations generally show lower total energies, which implies that all the bare M$_2$C MXenes are stabilized in the T-type. The lattice parameters of all the T- and H-type M$_2$C are listed in Table S2. The lattice parameters in M$_2$C generally decrease with the increasing atomic number of M, which could be ascribed to M with a larger atomic number that has a smaller atomic radius. Further, the decomposition energies of the T-type M$_2$C into its potential competing phases are studied and provided in Table S5. Most of the structures are metastable, which show negative decomposition energies, but their absolute values are smaller than 200 meV/atom. M$_2$C (M = Sm, Dy, Er, and Tm) show positive decomposition
energies, which imply that these configurations are thermodynamically stable. The dynamic stabilities of these T-type configurations are also evaluated. All the phonon dispersions of these configurations are calculated and provided in Figure 2. From this figure, the phonon frequencies in all the dispersions are observed to be positive, which implies that all the T-type M$_2$C configurations are dynamically stable. In addition, there are evident phonon gaps in these phonon dispersions, which could be ascribed to the remarkable difference in the mass of carbon and lanthanide atoms. The evident phonon gaps might enable the applications of these M$_2$C configurations in phononic crystals.

Based on the stable T-type configurations, spin-polarized band structures for all the M$_2$C configurations are calculated, and the corresponding results are provided in Figure S1 in Supporting Information. From the figure, all the bare M$_2$C MXenes are observed to be magnetic metals. The corresponding magnetic moments based on the unit cell of M$_2$C and the magnetic contribution from the f orbital in each M are provided in Table S4. Apparently, the magnetism of M$_2$C is mainly contributed by the f orbital. Further, the functionalized M$_2$C MXenes are studied. The functional group on MXene is dependent on the type of etchant with the selective etching approach. Using hydrofluoric acid as the
etchant, the surface of MXene is generally functionalized by the F and OH groups. Therefore, we focus on the fluorine and hydroxyl functional groups in this work. According to previous reports, the locations of functional groups could vary in different MXenes. To determine the stable functionalized structure, six possible configurations, as shown in Figure 3 are investigated. In this figure, the first and second rows present six different structural models of the fluorine- and hydroxyl-functionalized MXenes, respectively. To facilitate elaboration, the configurations from the left to the right side are denoted as model 1, 2, 3, 4, 5, and 6, respectively. In model 1, the functional groups are located on the top sites of the neighboring lanthanide atoms on both sides, while the groups are on the top sites of the bottom metals on both sides in model 2. In model 3, the functional groups are on the top sites of the central carbon atoms on both sides. In model 4, the functional groups are on the top sites of central carbon atoms on one side, which are on the top sites of the bottom metals on the opposite side. Regarding model 5, the groups are on the top sites of neighboring metals on one side, which are on the top sites of the hollow centers of neighboring metals on the other side. In the last model, the groups are on the top sites of neighboring metals on one side, which are on the top sites of the central carbon atoms on the opposite side. After structural relaxation, the relative total energies of these models for fluorine-functionalized MXenes are provided in Table 1, and the corresponding values for the hydroxyl-terminated structures are given in Table 2. From these tables, it is observed that model 2 shows the lowest energy for all the fluorine- and hydroxyl-functionalized configurations investigated. This stable configuration is similar to the structures of many other MXenes reported. Model 1 generally presents the highest energy, and model 4 shows a little higher value than that of model 2. Taking Ce₂C(OH)₂ as an example, the total energy of model 4 is only 0.180 eV higher than that of model 2.

Based on model 2, the thermodynamic stabilities of these lanthanide-based MXenes are further examined. According to eq 1, the formation energies for all the functionalized configurations are calculated and provided in Table 3. From the table, the formation energies of all the fluorine- and hydroxyl-terminated MXenes are observed to be negative. The negative values with the largest and smallest magnitudes are determined in Gd₂C(OH)₂ and Yb₂CF₂, which are −35.4 and −12.3 eV, respectively. These values with large magnitudes imply that the lanthanide-based MXenes are prone to be terminated by the fluorine and hydroxyl groups in hydrofluoric acid. The formation energy of the hydroxyl-terminated MXene generally shows a larger magnitude than that of the fluorine-functionalized structure, which implicates that the fluorine group could transform into the hydroxyl one upon washing and/or storing in water. Moreover, the magnitude of the formation energy of M₂CT₂ (T = F and OH) generally

Table 1. Relative Total Energies (in eV) of Fluorine-Functionalized MXenes M₂CF₂ (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb)

| MXenes     | model 1 | model 2 | model 3 | model 4 | model 5 | model 6 |
|------------|---------|---------|---------|---------|---------|---------|
| Ce₂CF₂     | 3.16    | 0.00    | 0.714   | 0.353   | 1.42    | 1.89    |
| Pr₂CF₂     | 3.14    | 0.00    | 0.746   | 0.368   | 1.44    | 1.93    |
| Nd₂CF₂     | 3.13    | 0.00    | 0.779   | 0.382   | 1.46    | 1.96    |
| Sm₂CF₂     | 3.12    | 0.00    | 0.845   | 0.406   | 1.48    | 2.01    |
| Eu₂CF₂     | 3.15    | 0.00    | 0.890   | 0.425   | 1.49    | 2.05    |
| Gd₂CF₂     | 3.08    | 0.00    | 0.906   | 0.422   | 1.48    | 2.04    |
| Tb₂CF₂     | 3.13    | 0.00    | 0.928   | 0.426   | 1.46    | 2.04    |
| Dy₂CF₂     | 3.02    | 0.00    | 0.946   | 0.427   | 1.45    | 2.09    |
| Ho₂CF₂     | 2.99    | 0.00    | 0.972   | 0.426   | 1.43    | 2.04    |
| Er₂CF₂     | 3.05    | 0.00    | 1.08    | 0.517   | 1.51    | 2.13    |
| Tm₂CF₂     | 2.93    | 0.00    | 0.997   | 0.422   | 1.40    | 2.04    |
| Yb₂CF₂     | 4.50    | 0.00    | 0.547   | 0.256   | 2.15    | 2.61    |

Table 2. Relative Total Energies (in eV) of Hydroxyl-Terminated MXenes M₂C(OH)₂ (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb)

| MXenes     | model 1 | model 2 | model 3 | model 4 | model 5 | model 6 |
|------------|---------|---------|---------|---------|---------|---------|
| Ce₂C(OH)₂ | 2.60    | 0.00    | 0.368   | 0.180   | 1.26    | 1.48    |
| Pr₂C(OH)₂ | 2.63    | 0.00    | 0.399   | 0.192   | 1.28    | 1.52    |
| Nd₂C(OH)₂ | 2.65    | 0.00    | 0.433   | 0.204   | 1.54    | 1.29    |
| Sm₂C(OH)₂ | 2.66    | 0.00    | 0.469   | 0.232   | 1.32    | 1.60    |
| Eu₂C(OH)₂ | 2.69    | 0.00    | 0.553   | 0.245   | 1.33    | 1.62    |
| Gd₂C(OH)₂ | 2.68    | 0.00    | 0.610   | 0.274   | 1.35    | 1.66    |
| Tb₂C(OH)₂ | 2.63    | 0.00    | 0.639   | 0.255   | 1.32    | 1.66    |
| Dy₂C(OH)₂ | 2.64    | 0.00    | 0.564   | 0.261   | 1.34    | 1.67    |
| Ho₂C(OH)₂ | 2.67    | 0.00    | 0.759   | 0.300   | 1.34    | 1.67    |
| Er₂C(OH)₂ | 2.61    | 0.00    | 0.632   | 0.305   | 1.33    | 1.70    |
| Tm₂C(OH)₂ | 2.63    | 0.00    | 0.810   | 0.262   | 1.60    | 1.28    |
| Yb₂C(OH)₂ | 3.64    | 0.00    | 0.302   | 0.136   | 1.83    | 2.05    |
increases, with its M from Ce to Gd, and then decreases from Gd to Yb. This behavior could be related to the occupation fraction of the f orbital of the lanthanide atom. Gd with half-full f electrons shows a stronger chemical bond with its surface group.

Further, the dynamic stabilities of these functionalized configurations are studied. The phonon dispersions of $M_2\text{CF}_2$ and $M_2\text{C(OH)}_2$ ($M = \text{Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb}$) are provided in Figures 4 and 5, respectively. All of the phonon dispersions except for that of Ce$\text{CF}_2$ are positive, implying that these configurations are dynamically stable. The hydroxyl-terminated structures generally show much higher frequencies than the corresponding fluorine-terminated members, which could be ascribed to the relatively light mass of the hydrogen element. Upon the same functional group, the highest phonon frequency also varies in different lanthanide-based MXenes. This is a reflection of different bond strengths in lanthanide-based MXenes as a stronger bond strength generally introduces a higher phonon frequency.

Based on the discussions above, most of the lanthanide-based MXenes investigated are thermodynamically and dynamically stable, which could be realized in further experiments.

To evaluate the magnetic stability of all the fluorine- and hydroxyl-terminated MXenes, nonmagnetic (NM), ferromagnetic (FM), and antiferromagnetic (AFM) states for the fluorine- and hydroxyl-terminated MXenes are examined. The structural diagrams of FM and AFM configurations are shown in Figure 6. The corresponding relative total energies for these NM, FM, and AFM configurations are presented in Table S5. Apparently, most FM configurations show the lowest total energies for these $M_2\text{CF}_2$ and $M_2\text{C(OH)}_2$ structures. Only Ho$\text{CF}_2$ and Dy$\text{C(OH)}_2$ show the lowest total energies in their AFM states. The energy difference between NM and FM is generally larger than that between FM and AFM. Eu$\text{CF}_2$ shows the largest energy difference between its FM and AFM states, which implies that this configuration might possess a high Curie temperature.

After checking the structural stabilities, the structural parameters are further investigated. The lattice parameters, layer thicknesses, and bond lengths for the fluorine-terminated MXenes are provided in Table 4, and the corresponding values for the hydroxyl-functionalized members are presented in Table 5. Apparently, the lattice parameters of both fluorine- and hydroxyl-terminated MXenes investigated here are generally larger than those of MXenes reported previously, which is due to the larger atomic radii of lanthanides than those of early transition metals. Moreover, the lattice parameters and bond lengths generally decrease with the increasing atomic number of lanthanides, which could be ascribed to the decreasing atomic radius of lanthanides. In particular, the Eu-containing MXenes are against this trend. Taking Eu$\text{CF}_2$ as an example, its lattice parameter of 3.74 Å is larger than that of 3.71 Å of its former Sm$\text{CF}_2$. The Eu–C bond is much larger than the other M–C bonds. Similar behaviors are also determined in the Eu$\text{C(OH)}_2$ MXene. These special structural parameters for Eu-containing MXenes increase...
could be caused by the special valence electron configuration of 4f\(^7\)5d\(^0\)6s\(^2\) in Eu. For the other lanthanide elements, except for Yb, the valence electrons are composed by 5d\(^1\)6s\(^2\) and varying numbers of 4f electrons. Generally, these predicted structural parameters will give some guidance for future synthesis and characterization of these lanthanide-based MXenes.

As mentioned previously, MXenes with their M elements in group IIIB generally show promising semiconducting properties; thus, the electronic properties of these lanthanide-based MXenes are further investigated. Based on the GGA-PBE functional, all the electronic structures for the fluorine- and hydroxyl-functionalized MXenes are provided in Figures 5 and 6, respectively. For the fluorine-terminated configurations, Ho\(_2\)CF\(_2\) is stabilized in its AFM states, as discussed previously, and its spin-up and spin-down states are degenerate in electronic structures. M\(_2\)CF\(_2\) (M = Ce, Tm, and Yb) are FM metals, and both the spin-up and spin-down states intersect with their Fermi levels. For the hydroxyl-terminated MXenes, Dy\(_2\)C(OH)\(_2\) is an AFM metal, while M\(_2\)C(OH)\(_2\) (M = Tb, Er, Tm, and Yb) are FM metals. Gd\(_2\)CT\(_2\) (T = F and OH) are the only two FM semiconducting members.

Table 4. Lattice Parameter \(a\), Layer Thickness \(h\), and Bond Lengths M–C and M–F (in Å) for M\(_2\)CF\(_2\) (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) MXenes

| MXenes   | \(a\) | \(h\) | M–C | M–F   |
|----------|-------|-------|-----|-------|
| Ce\(_2\)CF\(_2\) | 3.69  | 6.82  | 2.57 | 2.46  |
| Pr\(_2\)CF\(_2\) | 3.68  | 6.77  | 2.56 | 2.43  |
| Nd\(_2\)CF\(_2\) | 3.69  | 6.76  | 2.58 | 2.43  |
| Sm\(_2\)CF\(_2\) | 3.71  | 6.71  | 2.60 | 2.41  |
| Eu\(_2\)CF\(_2\) | 3.74  | 6.73  | 2.63 | 2.41  |
| Gd\(_2\)CF\(_2\) | 3.65  | 6.65  | 2.53 | 2.41  |
| Tb\(_2\)CF\(_2\) | 3.59  | 6.60  | 2.49 | 2.39  |
| Dy\(_2\)CF\(_2\) | 3.56  | 6.58  | 2.48 | 2.37  |
| Ho\(_2\)CF\(_2\) | 3.56  | 6.56  | 2.48 | 2.36  |
| Er\(_2\)CF\(_2\) | 3.54  | 6.53  | 2.48 | 2.35  |
| Tm\(_2\)CF\(_2\) | 3.52  | 6.51  | 2.47 | 2.33  |
| Yb\(_2\)CF\(_2\) | 3.54  | 6.58  | 2.51 | 2.33  |

Figures 7 and 8, respectively. For the fluorine-terminated configurations, Ho\(_2\)CF\(_2\) is stabilized in its AFM states, as discussed previously, and its spin-up and spin-down states are degenerate in electronic structures. M\(_2\)CF\(_2\) (M = Ce, Tm, and Yb) are FM metals, and both the spin-up and spin-down states intersect with their Fermi levels. For the hydroxyl-terminated MXenes, Dy\(_2\)C(OH)\(_2\) is an AFM metal, while M\(_2\)C(OH)\(_2\) (M = Tb, Er, Tm, and Yb) are FM metals. Gd\(_2\)CT\(_2\) (T = F and OH) are the only two FM semiconducting members.
determined here. All the rest of the configurations are half-metals. For these half-metals, it is worth pointing out that the metal state of the half-metal is spin-up when the atomic number of M in $M_2CT_2$ is smaller than that of Gd. On the contrary, the metal state of half-metal is spin-down when the atomic number of M is larger than that of Gd. This behavior might be related to the occupation fractions of f orbital in these lanthanide atoms. For example, the band gap of the spin-down states in Eu$_2$CF$_2$ is as large as 2.39 eV. This high spin-polarization in these half-metals enables these configurations in spintronic devices, especially for pure spin generation and injection.

Based on the GGA-PBE functional, the band gaps in Gd$_2$CF$_2$ and Gd$_2$C(OH)$_2$ are 0.732 and 0.400 eV, respectively. Apparently, the band gap of Gd$_2$C(OH)$_2$ is smaller than that of the fluorine-terminated configuration. The band gap in Gd$_2$CF$_2$ is indirect, with the valence band maximum (VBM) in its electronic energy band located at the BZ center, and the corresponding conduction band minimums (CBMs) lie on the high-symmetry M point. Gd$_2$C(OH)$_2$ is a direct band gap semiconductor, with both its VBM and CBM located at the BZ center. As the GGA-PBE functional generally underestimates the band gaps for semiconductors, the more precise HSE06 functional is also adopted. The electronic energy bands of Gd$_2$CT$_2$ (T = F and OH) from HSE06 are provided in Figure 9. Both the band gaps of Gd$_2$CF$_2$ and Gd$_2$C(OH)$_2$ increase significantly after the HSE06 correction. For Gd$_2$CF$_2$, its band gap increases from the GGA of 0.732 to 1.381 eV. This value is a little higher than the band gap of bulk silicon, implying that Gd$_2$CF$_2$ is suitable for semiconductor devices. For Gd$_2$C(OH)$_2$, its band gap increases to 0.882 eV after correction. On the basis of the direct and appropriate band gap, Gd$_2$C(OH)$_2$ could have promising applications in infrared adsorption devices. Moreover, these two structures are intrinsic 2D magnetic semiconductors, which are rarely reported in previous works. The properties of magnetic semiconductors indicate that Gd$_2$CT$_2$ (T = F and OH) have potential applications in the channel materials of spin devices and quantum computing.

In order to understand the origin of magnetism in these systems, the magnetic moments of the fluorine- and hydroxyl-terminated MXenes are calculated and listed in Tables 6 and 7.
respectively. The projected density of states (PDOS) of M in these lanthanide-based M$_2$CF$_2$ and M$_2$C(OH)$_2$ MXenes are calculated and show in Figures S2 and S3, respectively. Apparently, the magnetism is correlated with the occupation fraction of f orbitals in these M atoms, and their spin-up and spin-down states are separated in those FM configurations. Based on the unit cells, the magnetic moments vary significantly among these lanthanide-based MXenes. Yb$_2$C-(OH)$_2$ shows the lowest magnetic moment of 0.390 $\mu_B$. The largest magnetic moment is determined in Gd$_2$CF$_2$, the value of which is as large as 13.8 $\mu_B$. The total magnetisms in M$_2$CF$_2$ (M = Dy and Ho) and M$_2$C(OH)$_2$ is zero because their stable magnetic configurations are all in the AFM states. Apparently, the magnetism is correlated with the occupation fraction of f orbitals in Gd. This behavior could be directly seen from the magnetic contributions of f orbitals listed in Tables 6 and 7. The magnetic moment of each Gd atom contributes 6.84 $\mu_B$ in both Gd$_2$CT$_2$ (T = F and OH) generally show large magnetic moments because the f orbital in Gd is half-full. These high magnetic moments could enable these lanthanide-based MXenes’ applications in information storage, especially in 2D electronic devices.

Figure 8. (a−k) Electronic energy bands of M$_2$C(OH)$_2$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) MXenes based on the GGA-PBE functional. The Fermi level is set as 0 eV.

Figure 9. (a,b) Electronic energy bands of Gd$_2$CF$_2$ and Gd$_2$C(OH)$_2$ after the HSE06 correction. The Fermi energy is set as 0 eV.

Table 6. Magnetic Moments (in $\mu_B$) of M$_2$CF$_2$ (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) MXenes

| MXenes | total magnetization | M(f-orbital) |
|--------|--------------------|--------------|
| Ce$_2$CF$_2$ | 1.33 | 0.628 |
| Pr$_2$CF$_2$ | 3.75 | 1.88 |
| Nd$_2$CF$_2$ | 5.87 | 3.05 |
| Sm$_2$CF$_2$ | 10.1 | 5.31 |
| Eu$_2$CF$_2$ | 12.3 | 6.43 |
| Gd$_2$CF$_2$ | 13.8 | 6.84 |
| Tb$_2$CF$_2$ | 11.8 | 5.83 |
| Dy$_2$CF$_2$ | 9.77 | 4.77 |
| Ho$_2$CF$_2$ | 0.00 | $\pm$3.69 |
| Er$_2$CF$_2$ | 5.72 | 2.67 |
| Tm$_2$CF$_2$ | 3.53 | 1.60 |
| Yb$_2$CF$_2$ | 0.458 | 0.190 |
Table 7. Magnetic Moments (in $\mu_B$) of $M_2C(OH)_2$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) MXenes

| MXenes | total magnetization | $M(f$-orbital) |
|---------|---------------------|----------------|
| Pr$_2$C(OH)$_2$ | 3.68 | 1.85 |
| Nd$_2$C(OH)$_2$ | 5.82 | 3.02 |
| Sm$_2$C(OH)$_2$ | 10.1 | 5.29 |
| Eu$_2$C(OH)$_2$ | 12.3 | 6.42 |
| Gd$_2$C(OH)$_2$ | 13.7 | 6.84 |
| Tb$_2$C(OH)$_2$ | 11.8 | 5.86 |
| Dy$_2$C(OH)$_2$ | 0.00 | ±4.79 |
| Ho$_2$C(OH)$_2$ | 7.74 | 3.75 |
| Er$_2$C(OH)$_2$ | 5.69 | 2.69 |
| Tm$_2$C(OH)$_2$ | 3.48 | 1.60 |
| Yb$_2$C(OH)$_2$ | 0.390 | 0.161 |

As the hydroxyl-terminated MXenes have been demonstrated to show low work functions previously, the work functions of these lanthanide-based MXenes $M_2CT_2$ (M = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb; T = F and OH) are also investigated here. As shown in Figure 10, the hydroxyl-terminated MXenes generally show much lower work functions than the fluorine-terminated ones. The work functions of the fluorine-functionalized structures are in the range from 3.62 to 4.24 eV, with the minimum and maximum values determined in Pr$_2$CF$_2$ and Yb$_2$CF$_2$, respectively. With respect to the hydroxyl-terminated configurations, the corresponding values are in the range from 1.46 to 2.17 eV. These values are generally lower than 2.1 eV of the typical low work function material cesium. The lowest work function is determined in Tm$_2$C(OH)$_2$. Noteworthily, the work functions in several hydroxyl-terminated configurations are even lower than that in Sc$_2$C(OH)$_2$, which was found to be the lowest work function material reported previously. The low work function in these hydroxyl-terminated MXenes could be ascribed to the high potential of surface hydrogen atoms. Based on these low work functions, these lanthanide-based MXenes could have potential applications in field emitter cathodes.

**CONCLUSIONS**

In summary, the stabilities, structural parameters, and electronic properties of lanthanide-based MXenes have been investigated in this work. According to the formation energies and phonon dispersions calculated, most fluorine- and hydroxyl-terminated MXenes are stable. The fluorine- and hydroxyl-terminated MXenes are generally magnetic, and most of them are half-metals. High spin polarization has been determined in these half-metals. The spin-up states in the half-metal Eu$_2$CF$_2$ show a large band gap of 2.39 eV, Gd$_2$CT$_2$ (T = F and OH) are the only two magnetic semiconductors. From HSE06, it is observed that Gd$_2$CF$_2$ is an indirect semiconductor with a band gap of 1.38 eV, while Gd$_2$C(OH)$_2$ shows a direct band gap of 0.882 eV. The magnetisms in these lanthanide-based MXenes are mainly related to the occupation fractions of 4f orbitals in the lanthanide atoms. Based on the half-full 4f orbital of Gd, both the unit cells of Gd$_2$CT$_2$ (T = F and OH) show magnetic moments higher than 13.7 $\mu_B$. Moreover, the hydroxyl-terminated structures generally show relatively low work functions. The work function in Tm$_2$C(OH)$_2$ is as low as 1.46 eV, which could be the lowest work function to the best of our knowledge. Based on these predicted magnetic half-metallic, and semiconducting properties, with low work functions, these lanthanide-based MXenes could have widespread potential applications such as in spintronics, quantum computation, near-infrared detectors, field effect transistors, information storage, and field emitter cathodes. We look forward to the synthesis of these lanthanide-based MXenes in future experiments.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c03964.

Relative total energies between the T- and H-type $M_2C$ MXenes; lattice parameters for the T- and H-type $M_2C$ MXenes; potential competing phases and the corresponding decomposition energies for the T-type $M_2C$ MXenes; electronic energy bands for the T-type $M_2C$ MXenes based on the GGA-PBE functional and the corresponding magnetic moments and relative total energies between the NM, FM, and AFM states of the $M_2CT_2$ MXenes; and PDOS of M in $M_2CF_2$ and $M_2C(OH)_2$ MXenes (PDF)

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