Electronic Structure and Magnetic Anisotropy of Single-Layer Rare-Earth Oxybromide

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ABSTRACT: The discovery of intrinsic magnetism in two-dimensional (2D) limit has triggered increasing investigations in layered magnetic materials. However, most of the available candidates involves 3d transition metals, while the layered rare-earth magnetic materials are largely unexplored at present. Here, we proposed a series of 2D rare-earth magnetic semiconductors REOBr (RE = Tb, Dy, Ho, Er and Tm) with large magnetic moments and magnetic anisotropy energies using the PBE + U method. Our calculations indicate a half-metallic meta-stable state and a low-energy semi-conducting ground state in these 4f single-layers, which can be characterized by the location of the two-fold degenerate $x(x^2 - 3y^2)$ orbital. The dynamical stability of single-layer REOBr is further confirmed using phonon dispersions. The predicted energy gaps ranging from 2.47 to 4.26 eV decrease with the atomic number of the rare-earth element. Meanwhile, very large spin moments and orbital moments up to 6.018 and 2.872 $\mu_B$ are found, which seem to be insensitive to the magnetic state. Furthermore, the magnetic anisotropy energies are evaluated and understood by a fourth-order non-uniaxial anisotropy mode. Diverse anisotropy energy landscapes including easy cone, easy plane, and easy axis are found, and an extremely high magnetic anisotropy energy of about 8 meV per RE atom is found in the single-layer DyOBr. Our investigations provide a unique insight into layered rare-earth magnetic materials and suggest the single-layer REOBr as competing candidates for low-dimensional data storage applications.

1. INTRODUCTION

The low-dimensional magnetic materials have received considerable attention because of their potential application in information storage and processing. Especially, the discovery of intrinsic magnetism in bilayer Cr$_7$Ge$_2$Te$_6$ and single layer Cr$_3$x$_2$ has triggered increasing interest in layered magnetic materials. Because of the localized 3d states with strong correlation, it is quite likely to seek out a robust magnetism in transition-metal compounds (TMC). Nowadays, a large number of two-dimensional magnetic TMCs have been proposed both theoretically and experimentally.\textsuperscript{3-5} Moreover, a novel quantum confinement effect such as layer-dependent interlayer magnetic order is also revealed.\textsuperscript{6}

Besides the TMC, rare-earth compounds are also of particular importance in modern magnets. Rare-earth magnets are well known to be strong permanent magnets with transition temperatures above room temperature, strong magnetic anisotropy, and large magnetic moments.\textsuperscript{10} Layered rare-earth compounds also constitute another large family of magnetic materials, which offer an excellent host for the exfoliation into single-layer nanosheets. However, because of the limit of common LDA/GGA calculation for 4f electron, the knowledge of layered rare-earth based compound is quite limited at present.

In the present work, we focus on a series of layered tetragonal rare earth oxybromides REOBr, which are known as promising candidates for luminescence. REOBr crystallizes in the Matlockite (PbFCl) type tetragonal crystal structure with the space group of P4/nmm (no. 129).\textsuperscript{11} By spectroscopic investigations\textsuperscript{12,13} and magnetic susceptibility measurements,\textsuperscript{14} the crystal field parameters and effective magnetic moment of rare earth oxybromides were determined. These results also suggest that all REOBr show paramagnetic Curie–Weiss behavior at high temperatures above 100 K. Based on the observed negative Weiss constants, antiferromagnetic ordering was expected for all REOBr although such an ordering is only found in SmOBr and DyOBr. However, further experimental verification about magnetic properties is absent. Moreover, the detailed knowledge about the electronic structure and magnetic anisotropy of REOBr are also lacking. Earlier experimental investigations including energy transfer and migration studies have also suggested that REOBr exhibit 2D electronic and magnetic behavior.\textsuperscript{14} Moreover, the materials with similar crystal structures such as CrSBr and CrOBr have been proposed as 2D magnetic materials recently.\textsuperscript{15,16} It is thus
necessary to explore the magnetic properties of 2D REOBr and reveal their underlying mechanism.

Here, we performed a comprehensive first-principles calculation on layered REOBr (RE = Tb, Dy, Ho, Er and Tm), in which rare-earth element contains more than half full 4f electrons. The DFT + U method is also used to obtain reasonable electronic structures. An orbital-based strategy is proposed to overcome the multi-minima problem generally existed in a 4f electron system. The phonon dispersion is calculated to confirm the stability of a single layer. Moreover, the electronic structure and magnetic properties are evaluated in detail, and the magnetic anisotropy constants are extracted by fitting the direction-dependent energies to the non-uniaxial anisotropy model with fourth-order expression. The obtained geometries, electronic structures, and magnetic properties are then compared with available experimental and theoretical results. Our calculations show that REOBr are stable two-dimensional magnetic semiconductors with large magnetic moment and magnetic anisotropy energies.

2. RESULTS AND DISCUSSION

As shown in Figure 1, bulk REOBr possesses the layered tetragonal crystal structure with space group P4/nmm (no.129), in which the REOBr layers were stacked along c-axis. This implies that they exhibit quasi-2D nature of electronic and magnetic behavior and a single-layer can be exfoliated from their bulk crystal. We thus focus on single-layer REOBr in our investigations.

2.1. Multi-Minima Problem. The multi-minima problem is known to be a serious challenge in the first-principles investigation of 4f electron. In order to obtain the possible ground state, we calculate the total energies of system as a function of lattice parameters. During our calculations, many meta-stable electronic states are found. The achieved solutions at one particular lattice constant is then used to initialize the calculations at a neighboring lattice constant. As an illustration example, we present the results of HoOBr calculated using Perdew–Burke–Ernzerhof (PBE) and PBE + U methods in Figure 2. We can find two series of meta-stable states with distinct total energies and magnetic moments in both ferromagnetic and anti-ferromagnetic cases, which is independent on the calculation method. More interestingly, the ferromagnetic state always accompanies an anti-ferromagnetic states with close energies and magnetic moments. High (low)-energy states possess small (large) magnetic moment. Especially, low-energy FM and AFM states are almost degenerated.

In addition, these solutions also have different electronic structures. As shown in Figure 3, PBE + U calculations indicate a sizeable band gap of 3.596 and 3.653 eV in low-energy FM and AFM solution, respectively. However, a few bands in spin-up direction are found to cross the Fermi level in high energy states, indicating a half-metallic state. PBE calculations also give low-energy semiconducting and high-energy half-metal states, but the predicted band gaps of 0.693 and 0.872 eV in semiconducting states are smaller. Further analysis indicates that the Ho-4f electron orbital is quite localized and predominate the states of the conductive band minimum (CBM) as shown in Figure 4. It is interesting to notice that...
DOS of Ho-4f electronic states in the Fermi level is very high, implying the instability of half-metal states, while in the case of low-energy states, the Ho-4f electron shows a hybridization between Br-p and O-p orbital near valence band maximum (VBM).

In order to reveal the underlying mechanism and track the issues of multi-minima, we also analyze the orbital resolved DOS of Ho-4f electrons. 2D HoOBr has a point group of $C_{4v}$, in which the R$^{3+}$ ion is coordinated to four oxygen and four bromides atoms. According to group theory, the f electron will be spitted into $a_1 (z^2)$, $b_1 (x^2 - y^2)$, $b_2 (xyz)$, $e (x(x^2 - 3y^2), y(3x^2 - y^2), \{xz^2, yz^2\})$. As shown in the Figure 5, the energy levels of 4f electrons is very similar in FM and AFM cases, which leads to the degenerate energies shown above. Moreover, we also found that the two-fold degenerate $e (x(x^2 - 3y^2) \text{ and } y(3x^2 - y^2))$ orbital locates at the Fermi level in the high-energy half-metallic state. However, in the case of low-energy states, these orbitals were split into the occupied deep state around $-3 \text{ eV}$ and unoccupied states around $4 \text{ eV}$, which leads to a stable semiconductor states with much lower energy. This is very similar with bonding and anti-bonding state in the molecular orbital diagram, when several atoms get together to form molecules. In addition, the $xyz$ in the spin-down direction jumps from about $3 \text{ eV}$ in high-energy state to $-4 \text{ eV}$ in low-energy states, which furthers lower the total energy of low-energy states. As shown above, the states with different energy and electronic structures can be attributed to distinct orbital characters. This orbital-based strategy is thus suggested as a possible solution to overcome the multi-minima problem generally existed in 4f electron system, which may be helpful to identify low-energy solution in the other rare-earth compounds.

Because the on site coulomb interaction parameter $U$ is crucial for DFT + $U$ calculations, taking HoOBr as an illustrative example, we have also examined the effect of $U$ on the various properties of REOBr. The detailed the energy difference $\Delta E$ between low-energy FM and AFM states, the band gap, and magnetic moment of Ho atoms are shown in Table 1. These results indicate that a large band gap and the magnetic moment of the Ho element can be found, although their values increase with $U$. On the other hand, we can also find that $\Delta E$ is positive at $U-J = 2 \text{ eV}$ but kept negative when $U-J$ is larger than $3 \text{ eV}$. Because of the very strong correlation interaction of rare-earth ions, we choose a relatively large effective $U-J$ of $6 \text{ eV}$ for all rare-earth elements.

2.2. Structure, Stability, and the Electronic Structure. Using the orbital-based strategy established in HoOBr, we further clarified the possible ground state of the other XOBr monolayer using PBE + $U$ functional. The predicted equilibrium lattice parameters, independent to the magnetic state, decrease with atomic number of RE atoms with an exception of Er$^{3+}$. The tendency is consistent with the experiment$^{11,14}$ and can be attributed to the reduced RE$^{3+}$ ionic radius with the atomic number.$^{17}$

We have calculated the cleavage energy of REOBr following our pervious procedure for layered CrX$_3$.$^9$ To consider the interlayer vdW interaction, vdW functional in the form of
It should be noticed that only collinear magnetic structures were considered in the calculation, and other complex non-collinear magnetic structures such as spin-spiral states cannot be ruled out in the REOBr system. Considering the competitive stability between FM and AFM phase, we thus discuss the properties of single-layer REOBr in both states.

We further investigate the electronic structures of single-layer REOBr. Because of the heavy rare earth element, the spin–orbital coupling effect is also considered in the calculation for comparison. As shown in Table 2, the band gaps of ferromagnetic REOBr decrease from 4.221 (Tb), 3.522 (Dy), 3.354 (Ho), 3.088 (Er) to 2.476 eV (Tm), while the corresponding energy gaps for anti-ferromagnetic are 3.522(Dy), 3.354(Ho), 3.088(Er) to 2.476 eV (Tm), and this indicates that the exfoliation of single layers from bulk REOBr is feasible experimentally. To further confirm the stability of free-standing single-layer REOBr, we have also calculated the phonon dispersion. As shown in Figure 6, there are essentially no imaginary frequencies in the whole Brillouin zone in REOBr, which indicates that these single layer materials are dynamically stable and can exist as freestanding 2D crystals. According to the acoustic sum rule, acoustic mode frequencies at Γ point must be zero. Very small imaginary frequency near Γ point can be attributed to the numerical noise.

We also compare the difference between magnetic states of single-layer REOBr. As shown in the Table 2, we can find that AFM is the favorable ground state in the case of Tb and Dy, while the total energy of FM state seems to be lower in the case of Ho, Er and Tm. It should be noticed that the energy difference between ferromagnetic and anti-ferromagnetic state is very tiny, which implies the low magnetic transition temperature. It should be noticed that only collinear magnetic structures were considered in the calculation, and other complex non-collinear magnetic structures such as spin-spiral states cannot be ruled out in the REOBr system. Considering the competitive stability between FM and AFM phase, we thus discuss the properties of single-layer REOBr in both states.

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### Table 1. Energy Difference ($\Delta E = E_{FM} - E_{AFM}$), the Band Gap, and Magnetic Moment of HoOBr as a Function of the On Site Coulomb Interaction Parameter

| $U$–$J$ (eV) | TbOBr | DyOBr | HoOBr | ErOBr | TmOBr |
|-------------|-------|-------|-------|-------|-------|
| $\Delta E$ (eV) | 0.0023 | 0.0036 | 0.0059 | 0.0078 | 0.0095 |
| band gap (FM) (eV) | 2.0667 | 2.8159 | 3.1992 | 3.5962 | 4.0332 |
| magnetic moment (FM) ($\mu_B$) | 3.943 | 3.972 | 3.999 | 4.026 | 4.055 |
| band gap (AFM) (eV) | 2.1282 | 2.8496 | 3.2408 | 3.6425 | 4.0562 |
| magnetic moment (AFM) ($\mu_B$) | 3.943 | 3.974 | 4.003 | 4.032 | 4.062 |

### Table 2. Calculated Lattice Parameter, Energy Gap, Spin Moment, Orbital Moment, and Energy Difference between FM and AFM of Single-Layer REOBr

| $a$(Å) | TbOBr | DyOBr | HoOBr | ErOBr | TmOBr |
|-------|-------|-------|-------|-------|-------|
| $\Delta E$ (meV) | 1.662 | 0 | −8.442 | 0 | −2.152 |
| MAE (meV) | 0.233 | 0.994 | 0.708 | 0.224 | 0.246 |
| $K_1$ (meV/atom) | −0.344 | −0.834 | −0.673 | 0.214 | 0.234 |
| $K_2$ (meV/atom) | 0.427 | −0.132 | −0.032 | 0.008 | 0.008 |
| $K''$ (meV/atom) | 0.062 | 0.020 | 0.004 | 0.002 | 0.002 |
| easy axis (001) | 111 | 110 | 110 | 110 | 110 |

optB88-vdW were used. The calculated cleavage energies of ReOBr range from 0.20 to 0.34 J/m$^2$, which are comparable with CrX$_3$ (0.28 to 0.30 J/m$^2$) and smaller than experimentally estimated value for graphite (0.36 J/m$^2$). This indicates that the exfoliation of single layers from bulk REOBr is feasible experimentally. To further confirm the stability of free-standing single-layer REOBr, we have also calculated the phonon dispersion. As shown in Figure 6, there are essentially no imaginary frequencies in the whole Brillouin zone in REOBr, which indicates that these single layer materials are dynamically stable and can exist as freestanding 2D crystals.
and can be seen as a perturbation of the energy level of free ions. With the increasing atomic number of RE, the CBM gets closer to the Fermi-level, resulting in a reduced band gap. When the SOC effect is included, the gaps decrease with an amplitude of 0.2–0.3 eV. This value is comparable to the typical single-electron SOC strength of 4f electrons\textsuperscript{10} but seems to be smaller than Al\textsubscript{3} (A = Bi, Sb, As),\textsuperscript{19,20} where a large energy difference above 1 eV induced by SOC was found.

2.3. Magnetic Moment and Anisotropy. We now focus on the magnetic properties of single-layer REOBr. Our calculations indicate that the magnetic moment and magnetic anisotropy energy seem to be insensitive to the magnetic phase, and we thus only discussed the case of FM. As shown in Table 2, the calculated spin magnetic moments of the ferromagnetic RE\textsuperscript{3+} ion are 6.018, 4.989, 3.944, 2.862, and 1.821 \(\mu_B\) from Tb to Tm, respectively, and the spin moment increases slightly in the case of the anti-ferromagnetic phase. This result can be explained based on the picture of free rare-earth ions. The electron configuration of free trivalent rare-earth ions is 4f\textsuperscript{n} \((n = 8, 9, 10, 11, 12)\). According to the Hund’s rule, the numbers of unpaired f electron are 6, 5, 4, 3, and 2 and the corresponding spin moments are 6, 5, 4, 3, and 2 \(\mu_B\), close to the calculation results. In addition, the calculated orbital moments are 1.039, 1.839, 2.667, 2.799, and 2.872 \(\mu_B\), which also agrees with the increasing spin orbital coupling effect with the atomic number of RE atoms.

Both spin and orbital magnetic moment are less than that of free ions, which is consistent with the experimental trend. As revealed in the susceptibility data, effective magnetic moments were also found to be less than the free ion value.\textsuperscript{14} On the other hand, our calculation results seem to be lower than experimental effective magnetic moments. This may be because the experimental data are evaluated based on the supposition that 4f orbital plays a little role in bonding. In the present work, we employ a standard potential, in which all 4f electrons are treated as valence states and the possible hybridization between 4f orbital with other orbital can be described spontaneously. The difference between the theory and the experiment implies the importance of hybridization of RE\textsuperscript{3+} in magnetic properties of the REOBr system.
The magnetic anisotropy energy of single-layer REOBr is given in fourth-order non-uniaxial anisotropy model as:

\[ E_a = K_2 \sin^2 \theta + K_4 \sin^4 \theta + K_4' \sin^4 \theta \cos 4\phi \]  

in which the \( \theta \) and \( \phi \) are the zenithal and azimuthal angles, that denote the direction of the magnetization relative to the \( c \)-axis. \( K_2 \) and \( K_4 \) are the second-order and fourth-order uniaxial anisotropy constant, whereas \( K_2' \) corresponds to fourth-order non-uniaxial anisotropy constant. We calculated the total energies of single-layer REOBr in all directions (\( \theta, \phi \)) with an interval of 15°, and then, the direction-dependent energy is fitted using eq 1 to get anisotropy constants.

Taking DyOBr as an illustrating example (Figure 9), we can find that the energy dependence on direction is well fitted by a fourth-order non-uniaxial anisotropy model. This indicates that the anisotropy contributions are not only higher-order but also non-uniaxial. The obtained anisotropy constants and MA energies are collected in Table 2. Our calculations predict easy plane\( \langle 100 \rangle \) for TbOBr shown in polar coordinates. The calculation and fitting results in \( xy \) and \( xz \) plane of FM states are shown in (a,b), respectively. The corresponding results for AFM states are shown in (c,d).

Therefore, the Br and O atoms should provide different crystal-field parameters \( A_2^2 \) with opposite sign. For cuboid with \( a > c \), in which \( A_2^2 \) negative, the negative 4f charges and the negative crystal-field charges repel each other, easy-axis (easy-plane) anisotropy is thus expected for prolate (oblate) ion. In contrast, easy-plane (easy-axis) anisotropy should be achieved for positive \( A_2^2 \).

As shown above, our calculations predict an easy plane anisotropy for DyOBr and HoOBr but an easy axis for TmOBr, which is consistent with the single-ion magnetic anisotropy model in a negative crystal field. This also implies the dominated contribution from Br atoms in these systems. However, this is not the case for TbOBr and ErOBr. Thus, the competition of crystal field contribution between Br and O ligands may complicate the magnetic anisotropy behavior of REOBr. In addition, it should be noticed that the historical treatment of rare-earth-containing systems was based on the magnetic anisotropy only.
assumption that the 4f orbitals play a little role in bonding. This deviation in TbOBr and ErOBr may be related to the hybridization of rare-earth ions with O and Br atoms near the Fermi level, as shown above. Similar discussions are also found in recent review about electromagnetic susceptibility anisotropy of lanthanide coordination complexes. 24

3. CONCLUSIONS

In summary, we have performed a comprehensive first-principles calculation on layered REOBr (RE = Tb, Dy, Ho, Er and Tm) using the DFT + U method. An orbital-based strategy is proposed to overcome the multi-minima problem. The phonon dispersion is then calculated to confirm the stability of single layer. Moreover, the electronic gap, magnetic moment, and magnetic anisotropy energy are evaluated in details and compared with available experimental and theoretical results. The magnetic anisotropy constants are extracted by fitting the direction-dependent energies to the anisotropy model with fourth-order expression. Our calculations predict that an intrinsic semi-conductivity, large magnetic moment, and magnetic anisotropy energies in single-layer REOBr, which promises them as competitive candidates for low-dimensional data storage application.

4. COMPUTATIONAL METHOD

All DFT calculations are performed using the Vienna Simulation Package code, 25, 26 within the projector augmented-wave method. 27, 28 General gradient approximation (GGA) in the PBE implementation 29 is adopted as the exchange correlation functional. Convergence tests have been performed carefully both for plane-wave cutoff energy and k point sampling. A plane-wave basis set with a cutoff energy of 600 eV is used in the calculations. The Brillouin-zone integration is carried out using a 16 × 16 × 1 Γ-centered Monkhorst–Pack grid 30 for single-layer REOBr. Atomic positions are optimized until the forces on each atom are smaller than 0.02 eV/Å. A vacuum spacing of 16 Å is used in the supercell to avoid interaction between images. The phonon calculations have been performed using the finite-displacement approach, as implemented in the Phonopy code, 31 in which a 4 × 4 × 1 supercell is employed.

Because of the self-interaction errors and the issue of local energy minima, 32 an accurate description of the partially filled 4f states is still a large challenge to the commonly-used LDA/GGA methods. “Open-core” approach was used to overcome this problem routinely in which the 4f electrons with the number equal to a free RE 31 ion were placed in the core. Consequently, hybridization of 4f orbitals is forbidden in such methods. In order to capture possible hybridization of rare-earth atoms with other species, we employ a standard potential for rare-earth element, in which all f electrons are treated as valence states. To take into account the electronic correlation of RE 31 electrons, a simple rotationally invariant DFT + U version proposed by Dudarev et al. 33 was used. The spin–orbit coupling effects are also considered in magnetic anisotropy energy and band structure calculations.

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Notes

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