Computational discovery of two-dimensional rare-earth iodides: promising ferrovalley materials for valleytronics

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Abstract

Two-dimensional Ferrovalley materials with intrinsic valley polarization are rare but highly promising for valley-based nonvolatile random access memory and valley filter devices. These ferromagnetic materials exhibit valleys at or near the Fermi level with intrinsic magnetism. The strong coupling between magnetism and spin–orbit coupling induces intrinsic valley polarization. Using Kinetically Limited Minimization, an unconstrained crystal structure prediction algorithm, and prototype sampling based on first-principles calculations, we have discovered new Ferrovalley materials, rare-earth iodides RI$_2$, where R is a rare-earth element belonging to Sc, Y, or La-Lu, and I is Iodine. The rare-earth iodides are layered and demonstrate either 2H, 1T, or 1T$_d$ phase as the ground state in bulk, analogous to transition metal dichalcogenides (TMDCs). The calculated exfoliation energy of monolayers (MLs) is comparable to that of graphene and TMDCs, suggesting possible experimental synthesis. The MLs in the 2H phase exhibit ferromagnetism due to unpaired electrons in d and f orbitals. Throughout the rare-earth series, d bands have valley polarization at K and $\bar{K}$ points in the Brillouin zone in the vicinity of the Fermi level. Large intrinsic valley polarization in the range of 15–143 meV without external stimuli is observed in these Ferrovalley materials, which can be enhanced further by applying an in-plane bi-axial strain. These valleys can selectively be probed and manipulated for information storage and processing, potentially offering superior performance beyond conventional electronics and spintronics. We further show that the 2H ferromagnetic phase of RI$_2$ MLs possesses non-zero Berry curvature and exhibits anomalous valley Hall effect with considerable anomalous Hall conductivity. Our work will incite exploratory synthesis of the predicted Ferrovalley materials and their application in valleytronics and beyond.

1. Introduction

Two-dimensional (2D) magnetism was an enormous challenge until it was successfully demonstrated in layered Cr$_2$Ge$_2$Te$_6$ [1] and CrI$_3$ [2]. Magnetism combined with electronic and optical properties could be exciting because it can lead to novel gateways for exploring magneto-electrical, magneto-optical, and valley properties in magnetic materials [3–7]. Recently, 2D magnetic materials have been used in novel magnetic devices to enhance the performance of existing devices, such as the development of novel magnetic tunnel junctions (Fe$_3$GeTe$_2$/hBN/Fe$_3$GeTe$_2$) [5], gate tunable Curie temperature in Fe$_3$GeTe$_2$ over an extensive range 100–300 K [6], and giant tunnel magnetoresistance in CrI$_3$ based heterostructures [7] to name a few. Certain 2D magnetic materials exhibit an extra valley degree of freedom for electrons to possess in addition to charge and spin, which can be leveraged for memory devices leading to faster and more efficient logic systems and next-generation storage devices beyond conventional electronics and spintronics. Valley polarization is central to successfully controlling and manipulating the valley degree of freedom, which requires breaking time-reversal and inversion symmetries. Since it was first observed and exploited in graphene [8], several approaches, such as optical pumping [9], magnetic
proximity effect [10, 11], magnetic doping [12], and external magnetic [13], or electric field [14] has been used to achieve valley polarization in transition metal dichalcogenides (TMDCs). However, these methods involve additional external complexity, such as strong interaction with magnetic substrates, dynamical processes for optical pumping, and external magnetic field, which is cumbersome for robust manipulation of valleys in device architecture.

2D Ferrovalley materials overcome this limitation as they possess intrinsic magnetism and valley polarization and can be used in valley-based devices. Due to strong magnetic exchange interaction and spin–orbit coupling (SOC), intrinsic valley polarization is induced, which can be controlled and manipulated without additional external complexity. A limited number of Ferrovalley materials has been discovered till date, namely LaI$_2$, PrI$_2$ [15], VSe$_2$ [16], GeSe [17], VAgP$_2$Se$_6$ [18], CeI$_2$ [19], LaBr$_2$ [20], LaBrI$_2$ [21], NbX$_2$ (X = S, Se) [22], NbBr$_4$ [23], TiV$_2$I$_6$ [24], MA$_2$Z$_4$ (M = Mo, W; A = C, Si, Ge; Z = N, P, As) [25] and GdI$_2$ [26].

Many promising candidate materials are yet to be explored and expanding the family to accelerate the research interest in fabricating valley-based electronic devices. Furthermore, newly discovered materials can be combined with other 2D materials to form novel heterostructures exhibiting long-range ferromagnetism, complex spin textures, optoelectronic properties, topological bands, and ferroelectricity. This work explores the chemically rich space of rare-earth iodide compounds for their Ferrovalley properties and valleytronics applications. Using unconstrained ground-state crystal structure prediction algorithm Kinetically Limited Minimization (KLM) and prototype sampling approach combined with first-principles calculations, we computationally predict several new two-dimensional Ferrovalley materials. Rare-earth iodides (in RI$_2$ stoichiometry, where R ranges from Sc, Y, or La-Lu) are stable layered materials with ground-state structure either in 2H, 1T, or 1T$_d$ phase, analogous to TMDCs. These materials are magnetic in bulk and monolayer (ML) form, except for YbI$_2$, which is NM. The 2H phase in ML form exhibits valley polarization in the 15–143 meV range due to strong magnetic exchange interaction and SOC. In the next few sections, we discuss the crystal structure, relative phase stability, exfoliation energy, electronic, magnetic, and anomalous valley Hall properties of predicted 2D RI$_2$ MLs.

2. Methods

The KLM, an unconstrained crystal structure prediction algorithm, which combines unbiased random sampling and sequential atomic perturbations based on ground-state energy derived from the first principle calculations, is employed to predict the crystal structure of RI$_2$ materials. The KLM method has successfully been employed for the discovery of novel ternary nitrides [27, 28], ternary oxynitrides [29], and recently 2D materials [15, 30]. The crystal structure search is performed over 100–150 independent seed structures with varying formula units from 1 to 4. The initial random seed structures and subsequent perturbations enforce the minimum interatomic distance between different atomic species, significantly reducing the configurational space and prohibiting the inclusion of unphysical structures. The list of minimum inter-atomic distances used in the crystal structure search is included in the supplementary information (SI). The crystal structure prediction demonstrates that the ground state of RI$_2$ materials is 2D, either in 2H, 1T, or 1T$_d$ phase for all the compounds. Additionally, prototype structure sampling of RI$_2$ materials in 2H, 1T, and 1T$_d$ phases are performed to determine the low-energy competing meta-stable phases. The possible magnetic configurations, ferromagnetic (FM), anti-ferromagnetic (AFM), and non-magnetic (NM) are also taken into account for the ground-state crystal structure search. To address the intrinsic magnetism in these materials, a $2 \times 2 \times 1$ supercell for the 2H phase, $2 \times 2 \times 2$ supercell for the 1T phase, and $1 \times 2 \times 1$ supercell for the 1T$_d$ phase is constructed such that each unit cell contains two layers. For the AFM configuration of the bulk phase, several possible magnetic configurations in the two layers, shown in figure S1 of SI, are considered. For FM and NM configurations, the respective unit cell is used to estimate the total energy. The magnetic configurations (both in-plane and out-of-plane) in the ML form (shown in figure S2 of SI) are also considered for determining the lowest energy ground state of the MLs.

The first-principles calculations are performed based on density functional theory with generalized gradient approximation (GGA) SCAN functional [31] as implemented in the Vienna ab initio simulation package [32, 33]. For faster convergence, GGA of Perdew, Burke, and Ernzerhof (PBE) functional [34] is used for crystal structure prediction. Further analysis is performed using SCAN functional on the determined structures. The interactions between ionic cores and valence electrons are described with projector-augmented-wave potentials [35, 36]. The $3d$, $4s$ orbitals of Sc, $4s$, $4p$, $4d$, $5s$ orbitals of Y, and $4f$, $5s$, $5p$, $5d$, $6s$ orbitals of La-Lu rare earth elements are treated as valence electrons. The van der Waal corrections are incorporated using the DFT-D3 method [37]. Energy cutoff of 520 eV for plane-wave basis set expansion and Γ centered $k$-mesh of $11 \times 11 \times 3$ for bulk, $11 \times 11 \times 1$ for MLs for 2H, 1T phases, $7 \times 12 \times 2$ for bulk, and $7 \times 12 \times 1$ for ML for 1T$_d$ phase are used for integration over the Brillouin zone. The atomic positions and lattice constant are optimized until forces are less than 0.01 eV Å$^{-1}$ on each atom, and total energy converges to less than $10^{-6}$ eV. A vacuum of 20 Å is used along the
out-of-plane direction for MLs to avoid interactions with its periodic images. The phonon band structure is computed using the density functional perturbation theory [38] as implemented in Phonopy code [39] using a $4 \times 4 \times 1$ supercell. The Berry curvature and anomalous Hall conductivity are calculated using the WannierTools package [40] with tight binding Hamiltonian extracted from WANNIER90 [41].

3. Results

3.1. Crystal structure

Unconstrained crystal structure search taking into account various possible magnetic configurations, is performed for all possible rare-earth iodides with the general formula $\text{RI}_2$, where $\text{R}$ is a rare-earth element from Sc, Y, or La-Lu and $\text{I}$ is Iodine. We find that rare-earth iodides in $\text{RI}_2$ stoichiometry are 2D layered materials either in trigonal prismatic (2H) phase belonging to $P6_3/mmc$ space group, octahedral (1T) phase belonging to $P\overline{3}m1$ space group, or distorted octahedral (1T$_d$) phase belonging to $Pmm2_1$ space group, as shown in figures 1(a)–(c), respectively, analogous to TMDCs. Additionally, the prototype structure sampling of $\text{RI}_2$ in the 2H, 1T, and 1T$_d$ phases shows the relative stability of the polytypes (see figure 1(d)). The 2H and 1T phases are composed of a hexagonal lattice with 2 and 1 formula unit (fu) per unit cell, respectively, as shown by dashed lines in figures 1(a) and (b). 1T$_d$ phase can be generated from 1T phase by reconstruction in a $2 \times 1$ orthorhombic cell composed of 4 fu per unit cell. The reconstruction originated from a dimerized line of rare-earth atoms that leads to a lower energy structure driven by distortion due to the Peierls transition mechanism [42, 43]. Similar distortion leads to the stability of the 1T$_d$ phase in TMDCs has also been observed [44, 45]. All three phases are layered structures with van der Waals interactions between two subsequent layers.
The equilibrium lattice parameters for each of the RI materials in three phases are determined and listed in Table 1. The lattice parameters lie in a very narrow range throughout the series (in-plane $a = 3.93\text{Å}$–$4.60\text{Å}$ and out-of-plane per layer $c = 6.86\text{Å}$–$8.18\text{Å}$), owing to a similar atomic radius of the rare-earth elements. The distortion of the 1T$_d$ phase is not locally stable for all materials. In the case of PrI$_2$, NdI$_2$, SmI$_2$, EuI$_2$, DyI$_2$, ErI$_2$ and TmI$_2$, the initial 1T$_d$ structure relaxes into the 1T structure, suggesting that the 1T$_d$ phase is not even meta-stable for these materials.

### 3.2. Phase stability

The relative phase stability of RI$_2$ bulk compounds is shown in Figure 1(d), where the phase stability is plotted in the space of $\Delta E_{2H-1T_d}$ on the x-axis and $\Delta E_{1T-1T_d}$ on the y-axis. The possible magnetic configurations, FM, AFM, and NM, are also considered for each RI$_2$ compound, and the magnetic ground-state of each case is given in Table 1. Several possible AFM configurations are considered in bulk consisting of two layers, shown in figure S1 of SI. Out of the 17 RI$_2$ compounds, ScI$_2$, PmI$_2$, and YbI$_2$ have 1T$_d$ as the ground-state, while 2H and 1T phases are meta-stable. The lowest energy structure of YI$_2$, LaI$_2$, CeI$_2$, GdI$_2$, TbI$_2$, ErI$_2$, and LuI$_2$ is the 2H phase, while 1T and 1T$_d$ are meta-stable phases except for ErI$_2$ where 1T$_d$ phase is unstable. For the case of PrI$_2$, NdI$_2$, SmI$_2$, EuI$_2$, DyI$_2$, HoI$_2$, and TmI$_2$, the ground-state is 1T$_d$ phase while the 2H phase is a meta-stable phase, while 1T$_d$ is a meta-stable phase only for HoI$_2$. For PrI$_2$, NdI$_2$, SmI$_2$, EuI$_2$, DyI$_2$, ErI$_2$, and TmI$_2$ lie on the x-axis in the phase stability plot, figure 1(d), the 1T$_d$ phase is unstable. For these compounds, the 1T$_d$ phase transforms into lower energy 1T phase upon structural relaxation, hence $\Delta E_{1T-1T_d} = 0$.

All the bulk RI$_2$ compounds have FM as the ground-state for magnetic configuration, except for DyI$_2$ and HoI$_2$, which exhibit AFM as the
ground-state, and YbI$_2$ is NM due to fully filled 4f orbitals. The $\Delta E_{2H-1T_2}$ and $\Delta E_{1T-1T_2}$ in table 1 show slight energy differences between different structural phases, which suggests that the synthesis of metastable phases may be possible at finite temperatures under appropriate experimental conditions. The thermodynamic stability of RI$_2$ against their competing phases, including the RI$_3$ phase, is investigated using convex hull analysis and computing the decomposition energy ($\Delta E_{D}$), shown in figures 1(c) and (f). The $\Delta E_{D}$ is defined as the energy difference of the lowest energy RI$_2$ phase from the convex hull formed by all the known phases (including elemental phase) between respective R and I atoms, schematically shown in figure 1(e) for Nd-I system. A negative $\Delta E_{D}$ suggests that the energy of the lowest energy RI$_2$ phase falls below the convex hull, as for NdI$_2$ in figure 1(e), and that it is stable against decomposition into its competing phases and can be experimentally synthesized, which is the case for all the RI$_2$ compounds predicted in this work (see figure 1(f)). It is to be noted that a three-dimensional phase of EuI$_2$ (space group 62 $Pnma$), which is already known [46], is lower in energy than the 1T-FM phase by 32 meV per fu. Towards I-rich conditions, the RI$_3$ phase is an important composition for a competing phase, as illustrated in figure 1(e). The ground-state energy of all the known phases in different stoichiometries is computed for the convex hull analysis. RI$_3$ compounds are known for all the rare-earth elements except for Eu, Gd, and Yb. Therefore, we perform crystal structure sampling for EuI$_3$, GdI$_3$, and YbI$_3$, using the KLM approach. We find that all three materials are stable with layered crystal structures belonging to space groups 2 ($P\bar{T}$), 162 ($P\bar{1}1m$), and 12 ($C2/m$) for EuI$_3$, GdI$_3$, and YbI$_3$, respectively. The crystallographic information file for EuI$_3$, GdI$_3$, and YbI$_3$ structures are available in SI.

Rare-earth iodides in RI$_3$ stoichiometry are also stable as layered materials, where rare-earth elements are in +3 oxidation state. However, this work shows that rare-earth elements in a low-valent +2 oxidation state are also stable. R$^{+2}$ has the electron configuration $[Ar]3d^{4}4s^2$ for Sc$^{+2}$, $[Kr]4d^55s^2$ for Y$^{+2}$, and $[Xe]4f^{16-14}5d^{1-6}s^2$ for R$^{+2}$ where R is La-Lu. From the electron configuration, one can say that the rare-earth elements are also early transition elements with zero or one d electron in the valence shell. As with other transition elements which exhibit a range of oxidation states, rare-earth elements in R$^{0}$, R$^{+1}$, R$^{+2}$ and R$^{+3}$ oxidation states are also expected to exist [47, 48]. Considering other transition metal ions with similar electron configurations, for instance, Hf$^{+3}$ and La$^{+2}$ have the same electron configuration of $[Xe]5d^56s^2$, Hf$^{+3}$ is known in several compounds [49]. Therefore, the stability of rare-earth elements in a less common +2 oxidation state is also expected, as shown in this work for RI$_2$ compounds.

### 3.3. Exfoliation energy

The exfoliation energy ($E_{exf}$) of MLs in different phases is calculated and listed in table 1 and also shown in figure 2(a). The exfoliation energy is computed by the relation [50],

$$E_{exf} = (E_{mono} - E_{bulk})/A$$

where $E_{mono}$ and $E_{bulk}$ are the energy of ML and bulk per fu, respectively, and A is the in-plane area of bulk. The calculated $E_{exf}$ of MLs are comparable to the exfoliation energy of graphene (12 meV Å$^{-2}$) [51] and MoS$_2$ (26 meV Å$^{-2}$) [52], advocating their mechanical exfoliation. The $E_{exf}$ of 2H and 1T phases ranges between 16–25 meV Å$^{-2}$, which is close to the exfoliation energies of TMDCs. The $E_{exf}$ of distorted octahedral (1T$_d$) phase is significantly lower than that in 2H or 1T phase and ranges between 7 and 10 meV Å$^{-2}$, which suggests that the MLs in 1T$_d$ phase are weakly bound to each other and are easily exfoliate. The 1T$_d$ phase is derived from the 1T phase, where two neighbor metal atoms distort the octahedra around them due to Peierls distortion [42, 43]. This increases the out-of-plane lattice parameter, effectively reducing adjacent layers’ binding, thereby decreasing the exfoliation energy.

### 3.4. Electronic properties of 2H-ML

The 2H phase in ML form is the ground-state for YI$_2$, LaI$_2$, CeI$_2$, GdI$_2$, TbI$_2$, ErI$_2$, and LuI$_2$, while 1T phase of PrI$_2$, NdI$_2$, SmI$_2$, EuI$_2$, DyI$_2$, HoI$_2$, and TmI$_2$ MLs is the ground-state and 1T$_d$ phase of ScI$_2$, PmI$_2$, and YbI$_2$ MLs has the lowest energy. The ground state structure is preserved for all the RI$_2$ compounds in bulk and ML phase, mentioned in tables 1 and 2, respectively. All the RI$_2$ MLs favor FM configuration as the lowest energy magnetic phase, except for YbI$_2$, which is NM. For DyI$_2$ and HoI$_2$, which exhibit AFM configuration as the lowest energy magnetic phase in bulk (table 1), favors FM configuration in the ML form (table 2). The net magnetic moment ($\mu_B$) per fu in the 2H-FM phase of MLs is mentioned in table 2. It is to be noted that the FM configuration in in-plane (FM$_x$ and FM$_y$) and out-of-plane (FM$_z$) directions of the ML is considered in the determination of the lowest energy magnetic phase of MLs. We observe that in-plane and out-of-plane magnetic configurations are nearly degenerate in MLs with energy difference less than 4 meV per fu for most cases, except for PrI$_2$ (34 meV fu$^{-1}$), SmI$_2$ (21 meV fu$^{-1}$), DyI$_2$ (103 meV fu$^{-1}$), HoI$_2$ (92 meV fu$^{-1}$), ErI$_2$ (133 meV fu$^{-1}$) and TmI$_2$ (8 meV fu$^{-1}$), which prefers in-plane magnetic orientation over out-of-plane magnetic orientation. The energy difference between the lowest energy phase and the 2H–FM configuration for different MLs, $\Delta E_{GS-2H,FM}$, is shown for comparison in table 2. The energy difference between stable and metastable phases, considering different magnetic configurations, is small (~100 meV fu$^{-1}$), suggesting that under suitable
experimental conditions or external perturbation, the 2H phase in ML form can potentially be synthesized for several of the RI$_2$ compounds. The dynamical stability of all RI$_2$ MLs in the 2H phase is demonstrated by the absence of negative frequencies in phonon dispersion plots, shown in figure S3 of SI.

The electronic band structure of RI$_2$ MLs in the 2H phase shows valley polarization and is interesting for valleytronics. Therefore, the discussion on the electronic properties of these compounds in this section will be focused on the 2H phase of MLs, unless otherwise stated. In the trigonal prismatic crystal field of 2H phase, each R atom is coordinated with 6 I atoms. The $d$ orbitals of R element split into three groups $a(d_{z^2})$, $e_1(d_{x^2−y^2})$, and $e_2(d_{x^2+y^2})$ with increasing energy as shown in figure 2(b). The 3$d_{z^2}$ of Sc and 4$d_{z^2}$ of Y and Zr are singly occupied in the spin-up channel giving rise to a magnetic moment of 1 $\mu_B$ per fu with FM ordering. For other RI$_2$ MLs, the partial occupancy of 4$f$ and 5$d$ orbitals give rise to magnetism in these MLs with magnetic moments given in table 2. Depending on the number of electrons in 4$f$ orbital, the 5$d_{z^2}$ orbital is either occupied or unoccupied but lies near the Fermi energy ($E_F$). Irrespective of the occupation of $d_{z^2}$ orbital, the dispersion of $d_{z^2}$ state near the $E_F$ gives rise to valleys at K and $\bar{K}$ points in the Brillouin zone. The electronic band structure of ScI$_2$, YI$_2$, GdI$_2$, and LuI$_2$ MLs in 2H—FM configuration, with and without SOC, is shown in figure 3. With SOC, ScI$_2$, YI$_2$, GdI$_2$, and LuI$_2$ MLs in 2H phase are FM semiconductors with band gap of 0.23 eV, 0.32 eV, 0.60 eV, and 0.19 eV, and magnetic moments of 0.7 $\mu_B$, 0.5 $\mu_B$, 7.4 $\mu_B$, and 0.5 $\mu_B$ per fu, respectively. The band structures of other RI$_2$ MLs in 2H phase are shown in figures S5–S8 of SI. ScI$_2$, YI$_2$, LaI$_2$, CeI$_2$, NdI$_2$, PmI$_2$, SmI$_2$, EuI$_2$, GdI$_2$, and LuI$_2$ MLs are FM semiconductors in 2H phase with small band gap varying from 0.08 eV (LaI$_2$) to 0.77 eV (EuI$_2$). PrI$_2$, TbI$_2$, DyI$_2$, HoI$_2$, ErI$_2$, and TmI$_2$ are FM metals due to partial occupation of 4$f$ and 5$d$ orbitals. YbI$_2$ is a NM semiconductor with a band gap of 0.31 eV, due to fully filled 4$f$ orbitals of Yb$^{4+}$. The indirect band gap $E_g$ of all the RI$_2$ MLs in 2H phase is given in table 2. The direct band gap at K, $E_{g,K}$ is also given in table 2 and schematically shown in figure 3(c). Without SOC,
the valleys at $K$ and $\Gamma$ are degenerate, as highlighted by dashed lines in figures 3(a)–(d). The SOC lifts the degeneracy, leading to a large spontaneous valley polarization ($\Delta E_{\text{valley}}$) of 89 meV, 103 meV, 143 meV and 118 meV in ScI$_2$, YI$_2$, GdI$_2$, and LuI$_2$ MLs respectively, also shown in figures 3(e) and (f). A large valley polarization is also seen in other RI$_2$ MLs varying in the range of 15–143 meV, as shown in their electronic band structures figures S5–S7 of SI, listed in table 2 and shown figure 2(c). The largest value of 143 meV for $\Delta E_{\text{valley}}$ is for GdI$_2$ ML which also possesses the largest magnetic moment of 7.4 $\mu_B$ in FM configuration. Although the indirect band gap in these MLs is small, there is a large separation between the valence band maximum at $K$ and conduction band minimum at $M$, ensuring the robustness of valleys against scattering by long-wavelength phonons. Therefore, these materials exhibit intrinsic magnetism in two dimensions and show large spontaneous valley polarization without external stimuli. Additionally, these valleys are spin-polarized and coupled to the magnetic ordering, i.e. the polarity of valleys can be reversed by changing the direction of intrinsic magnetism.

In order to leverage the Ferrovalley properties in these materials, the 2H-FM phase of these materials needs to be synthesized. Among the materials discovered YI$_2$, LaI$_2$, CeI$_2$, GdI$_2$, TbI$_2$, ErI$_2$ and LuI$_2$ exhibit the 2H-FM phase as the ground state both in bulk and ML form, and are more likely to easy experimental synthesis for exploring Ferrovalley property. However, the energy difference between the ground state and 2H-FM phase for other RI$_2$ MLs is small ($\sim$100 meV) as mentioned in table 2 as $\Delta E_{\text{GS} - 2H, FM}$. Under non-equilibrium conditions and finite temperature, the 2H-FM phase of other RI$_2$ materials can also be potentially synthesized for exploring Ferrovalley property. As mentioned above, the in-plane and out-of-plane magnetic orientations in several of the RI$_2$ MLs are nearly degenerate, we also compute the bandstructure of these MLs with in-plane magnetic orientations. The valleys are preserved even when the magnetic orientations of the rare-earth atoms are in-plane to that of the ML, as shown for the case of GdI$_2$ and LuI$_2$ in figure S9 of SI. It is to be noted that the valley at $\Gamma$ point in the band structures (figure 3) may hinder the easy accessibility and manipulation of valleys at $K$ and $\Gamma$ points. However, the effect of in-plane compressive strain on these MLs selectively reduces the energy of the valley state at $\Gamma$ point below the valleys at $K$ and $\Gamma$ points, as has been shown in the case of LaI$_2$ and PrI$_2$ [15], and for GdI$_2$ and LuI$_2$ in figure S10 of SI, paving the way for efficient accessibility of valley states at $K$ and $\Gamma$.

In certain cases, due to the relative ordering of 5$d_{z^2}$ and 4$f$ orbitals, the 5$d_{z^2}$ orbitals lie slightly away from $E_F$. Such as in case of PrI$_2$ ML the valley states...
are ∼1 eV below the $E_F$ (figures S5(c) and (g)), while for NdI$_2$ ML the valley states are ∼0.5 eV above $E_F$ (figures S6(c) and (g)). $E_F$ needs to be tuned to access the valley states in such cases. Such $E_F$ tuning has been successfully achieved in Bi$_2$Se$_3$, and Ca / Sn doped Sb$_2$Te$_3$:Se $^{53}$, without modifying the states near the $E_F$. The valleys in SmI$_2$, TbI$_2$, DyI$_2$ and TmI$_2$ MLs are difficult to access due to the presence of 4$f$ states near the $E_F$ (figures S5–S8). Nevertheless, we have included the valley polarization in table 2 and figure 2(c) for all the RI$_2$ MLs in 2H-FM configuration. The valley polarization can further be enhanced and tuned by the application of in-plane biaxial strain $^{15}$. The spin-polarized valleys give an extra degree of freedom for the electrons to possess, which can potentially be utilized for enhanced functionalities of next-generation devices. The traditional ferrovalley materials require an external source such as magnetic proximity effect $^{54}$, optical pumping $^{9}$, or magnetic field $^{13}$ to achieve valley polarization. In contrast, RI$_2$ Ferrovalley materials eliminate the need of any external effect and are easier to implement in device architecture, making them emerging materials for next-generation nonvolatile memory devices $^{55, 56}$.

It is worth mentioning that the value of valley polarization and position of 4$f$ and 5$d$ states of a rare-earth element is dependent on the exchange-correlation functional. For instance, when using the GGA functional of Perdew–Burke–Ernzerhof (PBE) $^{34}$, valley polarization of 10 meV and 55 meV is computed for LaI$_2$ and PrI$_2$ MLs respectively, compared to 28 meV and 35 meV using meta-GGA SCAN functional $^{31}$. The Hubbard potential parameter ($U$) often correctly describes crystal lattice and electronic properties of rare-earth or transition metal elements $^{57}$. However, the $U$ value is often used as a fitting parameter, and its value is ambiguous in describing the properties of a novel system. To avoid such ambiguity, we have reported the results based on SCAN functional, which better describes the properties of correlated systems than the PBE functional $^{58, 59}$. However, it is critical to mention here that although the quantitative description of valley polarization reported in this work may lie within a certain energy window due to the limitation of exchange-correlation functionals in the accurate description of 4$f$ and 5$d$ states of rare-earth elements, a qualitative description of the discovery of magnetism in two dimensions and Ferrovalley property in these materials and trends in valley polarization across the rare-earth series certainly holds true.

### 3.5. Anomalous valley hall effect

In 2D hexagonal magnetic systems with broken inversion and time-reversal symmetries, the charge carriers possess non-zero Berry curvature $\Omega_\nu(k)$ at $K$ and $\bar{K}$ points in the Brillouin zone, leading to valley contrasting features in electron transport, known as the anomalous valley Hall effect $^{8, 60–62}$. The impact of an external electric field on electron transport is investigated by calculating the out-of-plane ($z$) component of the Berry curvature using the Kubo formula $^{63}$:

$$\Omega_z(k) = -\sum_{m} \sum_{\nu \neq \nu'} \frac{2i m \langle \phi_{\nu m} | \nu | \phi_{\nu'} \rangle \langle \phi_{\nu m} | \nu' | \phi_{\nu m} \rangle}{(E_m(k) - E_{\nu}(k))^2},$$

where $m$ and $n$ are the band index for the occupied orbitals, $f(\nu)$ is the Fermi–Dirac distribution function for the $m$th band, $\nu(k)$ is the velocity operator of electrons along $x(y)$ directions, and $|\phi_{\nu m}\rangle$ are the periodic part of the Bloch wave functions with eigenvalues $E_{\nu m}(k)$ and $E_{\nu}(k)$ respectively. The variation of $\Omega_z(k)$ is opposite in sign and unequal in magnitude can be seen at $K$ and $\bar{K}$ points. Under the effect of an external in-plane electric field, $E$, the electrons in these MLs acquire velocity along the transverse direction, $v_{\perp} \sim E_{||} \times \Omega_z(k)$, giving rise to anomalous Hall conductivity ($\sigma_{xy}$). The $\sigma_{xy}$ is a function of the $E_F$ and is computed as follows:

$$\sigma_{xy} = \frac{e^2}{h} \int_{BZ} \frac{d^2k}{(2\pi)^2} f(k) \Omega_z(k)$$

where $f(k)$ is the Fermi–Dirac function as a function of reciprocal lattice wave vector $k$.

The $\sigma_{xy}$ of ScI$_2$, YI$_2$, GdI$_2$, and LuI$_2$ MLs as a function of the $E_F$ is shown in figure 4(e). The zero level means that the $d^5$ bands up to the valley (also highlighted in figure 3) are occupied, and $d^5$ bands are unoccupied. $\sigma_{xy}$ attains a large value when $E_F$ is negative and crosses the valleys. The similarity in the variation of $\sigma_{xy}$ in ScI$_2$, YI$_2$, GdI$_2$, and LuI$_2$ MLs is a direct consequence of the similar nature of $d_{z^2} - \bar{d}_{z^2}$ orbitals near the $E_F$. The variation of $\sigma_{xy}$ of all other RI$_2$ MLs is shown in figure S11 of SI. It is to be noted that the valleys at $\Gamma$ point do not contribute to $\Omega_z(k)$ or $\sigma_{xy}$, and therefore, these charge carriers will be undeflected in the transverse direction in a Hall setup. Due to significant anomalous Hall conductivity in these MLs, the charge carriers along valleys can selectively be controlled and manipulated for valleytronics applications.
4. Conclusions

The unconstrained ground-state crystal structure prediction algorithm and prototype sampling have been employed to discover 17 new 2D rare earth iodides (RI\(_2\) materials where R is a rare-earth element from Sc, Y, and La-Lu, and I is Iodine). All the bulk materials are layered and either have trigonal prismatic (2H-P6\(_3\)/mmc space group), octahedral (1T-P\(_3\)1m space group), or distorted octahedral (1T\(_d\)-Pnm\(_2\) space group) as the lowest energy phase. The stability analysis shows that all the compounds are thermodynamically stable. The exfoliation energy of MLs is comparable to graphene and TMDCs, suggesting possible mechanical exfoliation in the experiment. ScI\(_2\), YI\(_2\), LaI\(_2\), CeI\(_2\), NdI\(_2\), PmI\(_2\), SmI\(_2\), EuI\(_2\), GdI\(_2\), and LuI\(_2\) MLs in 2H phase are FM semiconductors with small band gap varying from 0.08 eV (LaI\(_2\)) to 0.77 eV (EuI\(_2\)). PrI\(_2\), TblI\(_2\), DyI\(_2\), HoI\(_2\), ErI\(_2\) and TmI\(_2\) MLs in 2H phase are FM metals, while YbI\(_2\) ML is an NM semiconductor. Newly discovered RI\(_2\) MLs exhibit large intrinsic valley polarization in the range of 15–143 meV in the 2H-FM phase, which can further be tuned and enhanced on the application of in-plane bi-axial strain. These materials are novel Ferrovalley materials, where electrons possess the additional valley degree of freedom along with charge and spin. Beyond conventional electronics and spintronics, these materials are emerging for next-generation electronic devices for information processing and data storage. We further show that these MLs exhibit the anomalous valley Hall effect with considerable anomalous Hall conductivity up to 15 S cm\(^{-2}\) with proper tuning of the Fermi level. Because of the rapid development of 2D materials and their applications, discovering new 2D materials with magnetism and large intrinsic valley polarization without external stimuli is significant for valleytronics applications. We believe our work will incite exploratory synthesis of these materials for applications in valleytronics and beyond.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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