A possible way to achieve anomalous valley Hall effect by piezoelectric effect in GdCl$_2$ monolayer

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Ferrovalley materials can achieve manipulation of the valley degree of freedom with intrinsic spontaneous valley polarization introduced by their intrinsic ferromagnetism. A good ferrovalley material should possess perpendicular magnetic anisotropy (PMA), valence band maximum (VBM)/conduction band minimum (CBM) at valley points, strong ferromagnetic (FM) coupling and proper valley splitting. In this work, the monolayer GdCl$_2$ is proposed as a potential candidate material for valleytronic applications by the first-principles calculations. It is proved that monolayer GdCl$_2$ is a FM semiconductor with the easy axis along out of plane direction and strong FM coupling. A spontaneous valley polarization with a valley splitting of 42.3 meV is produced due to its intrinsic ferromagnetism and spin orbital coupling (SOC). Although the VBM of unstrained monolayer GdCl$_2$ is away from valley points, a very small compressive strain (about 1%) can make VBM move to valley points. We propose a possible way to realize anomalous valley Hall effect in monolayer GdCl$_2$ by piezoelectric effect, not an external electric field, namely piezoelectric anomalous valley Hall effect (PAVHE). This phenomenon could be classified as piezo-valleytronics, being similar to piezotronics and piezophototronics. The only independent piezoelectric strain coefficient $d_{11}$ is -2.708 pm/V, which is comparable to one of classical bulk piezoelectric material $\alpha$-quartz ($d_{11}=2.3$ pm/V). The biaxial in-plane strain and electronic correlation effects are considered to confirm the reliability of our results. Finally, the monolayer GdF$_2$ is predicted to be a ferrovalley material with dynamic and mechanical stabilities, PMA, VBM at valley points, strong FM coupling, valley splitting of 47.6 meV, and $d_{11}$ of 0.584 pm/V. Our works provide a possible way to achieve anomalous valley Hall effect by piezoelectric effect, which may stimulate further experimental works related with valleytronics.

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I. INTRODUCTION

Rather than spin and charge, carriers in crystals are also endowed with the valley degree of freedom, which is useful to process information and perform logic operations (valleytronics)$^{1-6}$. Two or more local energy extremes in the conduction band or valence band, which are degenerate but inequivalent at the inequivalent k points in the momentum space, are needed for a valley material. To realize applications of valleytronics, the electrons or holes in different valleys must be selectively produced or manipulated. Although the possibility to achieve manipulation of the valley degree of freedom has been proposed in certain three-dimensional (3D) materials$^7$, the field of valleytronics is truly flourishing with the advent of two-dimensional (2D) materials.

The reduction in dimensionality of 2D materials results in that space inversion symmetry is often eliminated in 2D structures, allowing these materials to become piezoelectric$^8$, which is also very important for valleytronics described by Berry curvature $\Omega(k)$. In 2D hexagonal systems with broken space inversion symmetry, the Berry curvature in the K and -K valleys will be nonzero along the out of plane direction, and the Berry curvatures of two valleys are in opposite signs. If the time reversal symmetry is also broken, their absolute values are no longer identical, and the valley contrasting feature will be induced. Under an in-plane longitudinal electric field $E$, the Bloch electrons in these 2D systems will acquire an anomalous Hall velocity $v$ due to $v \sim E \times \Omega(k)^9$, and then the anomalous valley Hall effect will be produced, which can be achieved in ferrovalley materials$^{10}$. Many ferrovalley materials have been predicted, such as 2H-VSe$_2$$^{10}$, CrSi$_2$X$_4$ (X=N and P)$^{11}$, VAgP$_2$Se$_6$$^{12}$, LaBr$_2$$^{13,14}$, VS$_2$P$_4$$_{15}$, NbX$_2$ (X=S

FIG. 1. (Color online)Sketch of anomalous valley Hall effect under an in-plane longitudinal electric field $E$, and the $E$ is induced with uniaxial strain by piezoelectric effect. Upward arrows and downward arrows represent spin-up and spin-down carriers, respectively. Only one edge of the sample can accumulate the charge carriers, and another edge will accumulate ones, when reversing the magnetization orientation.
and Se\textsuperscript{16}, Nb\textsubscript{3}I\textsubscript{8}\textsuperscript{17}, TiV\textsubscript{16}\textsuperscript{18}. It is a natural idea to induce in-plane longitudinal electric field $E$ with an applied uniaxial in-plane strain by piezoelectric effect, and then anomalous valley Hall effect can be produced, which is illustrated in Figure 1.

To well achieve PAVHE, a 2D material should possess the strong FM coupling with PMA (The out-of-plane magnetization easy axis is important not only for FM order but also for valley behavior.), the appropriate energy band gap and valley splitting (The band gap and valley splitting should be large enough to overcome the thermal noise.), and the pure in-plane piezoelectric effect with only $d_{11}$ (The only independent $d_{11}$ means only in-plane longitudinal electric field.). Recently, a kind of exotic 2D ferromagnetic semiconductors GdX\textsubscript{2} (X=Cl, Br and I) based on rare-earth ions with f-electrons are predicted to have a large magnetization with high Curie temperature beyond 220 K\textsuperscript{19,20}. The monolayer GdCl\textsubscript{2} is predicted as a promising candidate material for valleytronics applications, which is spontaneously valley polarized with a giant splitting of 149 meV\textsuperscript{21}. However, GdI\textsubscript{2} possesses in-plane magnetic anisotropy, not PMA\textsuperscript{19,20}. Among GdX\textsubscript{2} (X=Cl, Br and I) monolayers, the easy axis of only monolayer GdCl\textsubscript{2} is along the out of plane direction\textsuperscript{20}. The monolayer GdCl\textsubscript{2} has $\overline{p}6m2$ point-group symmetry, which means that only independent $d_{11}$ is nonzero.

In light of PMA and independent $d_{11}$, monolayer GdCl\textsubscript{2} is likely to be a potential ferrovalley material to realize PAVHE. In this work, we investigate the valley physics and piezoelectric properties of monolayer GdCl\textsubscript{2} by the first-principles calculations. The monolayer GdCl\textsubscript{2} exhibits a pair of valleys in the valance band at the K and -K points with a valley splitting of 42.3 meV due to its intrinsic ferromagnetism and SOC. The predicted $d_{11}$ is -2.708 pm/V, which is comparable to one of $\alpha$-quartz ($d_{11}=2.3$ pm/V). To confirm the reliability of our results, the biaxial in-plane strain and electronic correlation effects on valley physics and piezoelectric properties are considered. Finally, the monolayer GdF\textsubscript{2} is predicted to be likely to be a potential ferrovalley material. Our works provide potential 2D valleytronic materials to achieve PAVHE for developing high-performance and controllable valleytronics.

The rest of the paper is organized as follows. In the next section, we shall give our computational details and methods. In the next few sections, we shall present structure and stability, electronic structure and valley Hall effect, and piezoelectric properties of monolayer GdCl\textsubscript{2}, along with strain and electronic correlation effects on its valleytronics and piezoelectric properties. Finally, we shall give our discussion and conclusions.

**II. COMPUTATIONAL DETAIL**

First-principles calculations with spin-polarization are performed within density functional theory (DFT)\textsuperscript{22}, as implemented in the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{23–25} within the projector augmented-wave (PAW) method. The generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) functional is used as the exchange-correlation interactions. The kinetic energy cutoff is set to 500 eV, and the total energy convergence criterion $10^{-8}$ eV is used. The optimized convergence criterion for atomic coordinates is less than 0.0001 eV Å\textsuperscript{-1} for force on each atom. The vacuum space is set to more than 18 Å to avoid adjacent interactions. The $18\times18\times1$ Monkhorst-Pack k-point mesh is used to sample the Brillouin zone for calculating electronic structures and elastic properties.

![Figure 2](image_url) FIG. 2. (Color online) The (a) top view and (b) side view of crystal structure of monolayer GdCl$(_2$). The red and black frames represent the rhombus primitive cell and rectangle supercell. The rectangle supercell is used to calculate the piezoelectric stress coefficients, whose width and height are defined as $x$ and $y$ directions, respectively.

![Figure 3](image_url) FIG. 3. (Color online) Calculated energy of AFM state and FM state of monolayer GdCl$(_2$) as a function of lattice constants $a$ with rectangle supercell.
and 10×20×1 Monkhorst-Pack k-point mesh for piezoelectric calculations. To account for the localized nature of 4f orbitals of Gd atoms, a Hubbard correction \( U_{\text{eff}} \) is employed within the rotationally invariant approach proposed by Dudarev et al., where \( U_{\text{eff}} \) is set as 4 eV, 5 eV, 8 eV\(^{19,20} \) for for monolayer GdCl\(_2\), GdBr\(_2\) and GdI\(_2\), respectively. The SOC is incorporated for self-consistent energy and band structure calculations. The elastic stiffness tensor \( C_{ij} \) are calculated by using strain-stress relationship (SSR) with GGA, and the piezoelectric stress tensor \( \varepsilon_{ij} \) are carried out by density functional perturbation theory (DFPT) method\(^{27} \) with GGA. The 2D elastic coefficients \( C_{ij}^{2D} \) and piezoelectric stress coefficients \( \varepsilon_{ij}^{2D} \) have been renormalized by \( C_{ij}^{2D} = L_z C_{ij}^{3D} \) and \( \varepsilon_{ij}^{2D} = L_z \varepsilon_{ij}^{3D} \), where the \( L_z \) is the length of unit cell along \( z \) direction. Within finite displacement method, the interatomic force constants (IFCs) of monolayer GdF\(_2\) are calculated based on the \( 5 \times 5 \times 1 \) supercell with FM ground state. Based on the harmonic IFCs, phonon dispersion spectrum of monolayer GdF\(_2\) is obtained by the Phonopy code\(^{28} \).

### III. Structure and Stability

The monolayer GdCl\(_2\) belongs to the hexagonal crystal system with 2H-MoS\(_2\) type structure, which contains one Gd atomic layer, sandwiched by two Cl atomic layers (See Figure 2). The corresponding point group is \( p\bar{6}m2 \) with broken inversion symmetry. The magnetic ground state of monolayer GdCl\(_2\) is determined by comparing the energies of antiferromagnetic (AFM) and FM states.
Figure 3. The easy axis of monolayer GdCl\textsubscript{2} can be random, and it is difficult to realize the long-range magnetic ordering in 2D materials, which can be described by magnetic anisotropy energy (MAE). The monolayer GdBr\textsubscript{2} and GdI\textsubscript{2} possess in-plane magnetic anisotropy\textsuperscript{19,20}. This means that the spin orientations of Gd atoms can be random, and it is difficult to realize the long-range magnetic ordering without external field. However, the easy axis of monolayer GdCl\textsubscript{2} is along out of plane direction\textsuperscript{20}. By considering SOC interaction, the MAE of monolayer GdCl\textsubscript{2} is calculated as the difference between the in-plane and out-of-plane magnetization stability energy, and the corresponding value is 93 μeV/Gd.

The thermal and dynamic stabilities of monolayer GdCl\textsubscript{2} have been proved by Ab initio molecular dynamics (AIMD) simulations and phonon dispersion\textsuperscript{20}. It is also important to check the mechanical stability of monolayer GdCl\textsubscript{2} by calculating elastic constants. Using Voigt notation, the elastic tensor \( C \) with \( \text{P6m2} \) point-group symmetry for 2D materials can be reduced into:

\[
C = \begin{pmatrix}
C_{11} & C_{12} & 0 \\
C_{12} & C_{11} & 0 \\
0 & 0 & (C_{11} - C_{12})/2
\end{pmatrix}
\]  (1)

The calculated results show that \( C_{11} \) and \( C_{12} \) are 45.95 Nm\textsuperscript{-1} and 13.53 Nm\textsuperscript{-1}, respectively. The calculated \( C_{ij} \) satisfy the Born criteria of mechanical stability\textsuperscript{20}: \( C_{11} > 0 \) and \( C_{11} - C_{12} > 0 \), which confirms the mechanical stability of monolayer GdCl\textsubscript{2}. Due to hexagonal symmetry, the monolayer GdCl\textsubscript{2} is mechanically isotropic. The 2D Youngs moduli \( C^{2D} \), shear modulus \( G^{2D} \) and Poisson’s ratio \( \nu^{2D} \) can simply be expressed as\textsuperscript{29}:

\[
C^{2D} = \frac{C_{11}^2 - C_{12}^2}{C_{11}}
\]  (2)

\[
G^{2D} = C_{66} = \frac{C_{11} - C_{12}}{2}
\]  (3)
The calculate Young’s moduli $C_{2D}$, shear modulus $G_{2D}$ and Poisson’s ratio $\nu$ are 41.97 Nm$^{-1}$, 16.21 Nm$^{-1}$ and 0.295, respectively. The $C_{2D}$ is less than that of graphene (340 Nm$^{-1}$), which indicates that monolayer GdCl$_2$ can be easily tuned by strain, being favorable for novel flexible piezotronics.

\[ \nu^{2D} = \frac{C_{12}}{C_{11}} \quad (4) \]

IV. ELECTRONIC STRUCTURE AND VALLEY HALL EFFECT

The electronic configuration of isolated Gd atom is $4f^{7}5d^{1}6s^{2}$. For monolayer GdCl$_2$, two electrons of one Gd atom are transferred to the six neighboring I atoms, and the electronic configuration of Gd becomes $4f^{7}5d^{3}$, which will introduce an $8 \mu_B$ magnetic moment. The calculated magnetic moment of Gd is 7.463 $\mu_B$, and the total magnetic moment per unitcell is $8 \mu_B$. The spin-polarized band structure of monolayer GdCl$_2$ without SOC is shown in Figure 4. The calculated results show that the monolayer GdCl$_2$ is a semiconductors with an indirect band gap of 0.91 eV. The VBM and CBM are provided by the majority spins and minority spins, and they locate at the $\Gamma$ and M high symmetry points, respectively. This makes monolayer GdCl$_2$ to be a bipolar magnetic semiconductor, which can generate 100% spin-polarized currents with inverse spin-polarization direction for electron or hole doping. It is clearly seen that the energy extremes of K and -K high-symmetry points are degenerate in the valence band (Figure 4 (d)), and monolayer GdCl$_2$ is a potential ferrovalley material.

The band structures of monolayer GdCl$_2$ with SOC for magnetic moment of Gd along the positive and negative z direction (out of plane) are also plotted in Figure 4. When the SOC is included, the degeneracy between the K and -K valley states is removed in the valence band, and a spontaneous valley polarization is induced with valley splitting of 42.3 meV, which is higher than or compared to ones of reported ferrovalley materials, such as VAgP$_2$Se$_6$ (15 meV)\textsuperscript{12}, LaBr$_2$ (33 meV)\textsuperscript{13,14}, TiVI$_6$ (22 meV)\textsuperscript{18}, VSi$_2$P$_4$ (49.4 meV)\textsuperscript{15} and 2H-VSe$_2$ (89 meV)\textsuperscript{19}. It is found that the energy of K valley state is higher than one of -K valley (Figure 4 (e)). It is interesting that an external magnetic field can tune valley polarization of monolayer GdCl$_2$. By reversing the magnetization of Gd atoms, the spin and valley polarization can be flipped simultaneously, and the energy of -K valley becomes higher than one of K valley (Figure 4 (f)). These mean that manipulating magnetization direction is an efficient way to tune the valley properties of the monolayer GdCl$_2$. Furthermore, the band related with valley properties is separated well from other energy bands. Although the VBM of monolayer GdCl$_2$ occurs at $\Gamma$ point, the K/-K valleys are still well defined and not far in energy. In fact, very small compressive strain (about 1%) can change VBM from $\Gamma$ to K/-K point (next section). As is well known, the GGA overestimates the lattice constants of materials, and the VBM of monolayer GdCl$_2$ may intrinsically locate at K/-K point.

The combined effects of the intrinsic magnetic exchange field and strong SOC give rise to the spontaneous valley polarization. When the spin polarization is performed without SOC, the spin-up and spin-down states are completely split by the magnetic exchange interaction, but he energy extremes of K and -K high-symmetry points are degenerate in the valence band. When the magnetic exchange interaction is absent, SOC still can induce spin nondegeneracy at both K and -K valley due to missing spatial inversion symmetry, but K and -K valleys are energetically degenerate with opposite spins because of existing time reversal symmetry. In a word, combined with high Curie temperature (224 K)\textsuperscript{20} and PMA, GdCl$_2$ is an ideal ferrovalley material for the valleytronic devices.

The valley Hall effect can be described by Berry curvature, and a nonzero Berry curvature along the out of plane direction can be attained in the K and -K valleys for hexagonal systems with broken space inversion symmetry. With the missing time reversal symmetry, the valley contrasting feature can be produced. To study these properties of monolayer GdCl$_2$, the Berry curvature is calculated directly from the calculated wave functions by using the VASP\textsuperscript{BERRY} code, which is based on Fukui’s method\textsuperscript{31}. The calculated Berry curvature distribution

FIG. 8. (Color online) Calculated Berry curvature distribution of monolayer GdCl$_2$ in the 2D Brillouin zone with $a/a_0$ being 0.94, 0.98 and 1.02 by using GGA+SOC.
of monolayer GdCl$_2$ in the 2D Brillouin zone without SOC and with SOC for magnetic moment of Gd along the positive and negative z direction are shown Figure 5. Without SOC, the Berry curvatures of K and -K valleys are in opposite signs, and the absolute values are the same. When the SOC is included, their absolute values of the Berry curvatures of K and -K valleys are no longer identical, which shows the typical valley contrasting properties. It is also found that the numerical values between K and -K valleys overturn, when the magnetic moment of Gd changes from the positive to negative z direction.

V. PIEZOELECTRIC PROPERTIES

The monolayer GdCl$_2$ with $p6m2$ point-group symmetry lacks inversion symmetry, but the reflectional symmetry across the xy plane still holds. These mean that only $e_{11}/d_{11}$ with defined x and y direction in Figure 2 is nonzero. This is the same with ones of MoS$_2$ monolayer, but is different from ones of Janus monolayer MoSSe with additional $e_{11}/d_{11}$.

For 2D materials, only considering the in-plane strain and stress equations, the piezoelectric stress and strain tensors by using Voigt notation can be reduced into:

$$
\begin{pmatrix}
    e_{11} & -e_{11} & 0 \\
    0 & 0 & -e_{11}
\end{pmatrix}
$$

(5)

$$
\begin{pmatrix}
    d_{11} & -d_{11} & 0 \\
    0 & 0 & -2d_{11}
\end{pmatrix}
$$

(6)

When a uniaxial in-plane strain is imposed, the in-plane piezoelectric polarization ($e_{11}/d_{11}$) can be calculated by $e_{ik} = d_{ij}C_{jk}$:

$$
d_{11} = \frac{e_{11}}{C_{11} - C_{12}}
$$

(7)

TABLE I. For monolayer GdX$_2$ (X=F, Cl, Br and I), the elastic constants $C_{ij}$ in Nm$^{-1}$, the piezoelectric stress coefficients $e_{11}$ with electronic part $e_{11e}$ and ionic part $e_{11i}$ in $10^{-10}$ C/m, and the piezoelectric strain coefficients $d_{11}$ in pm/V.

| Name   | $C_{11}$ | $C_{12}$ | $e_{11e}$ | $e_{11i}$ | $e_{11}$ | $d_{11}$ |
|--------|----------|----------|-----------|-----------|----------|---------|
| GdF$_2$ | 73.87    | 19.61    | 1.365     | -1.048    | 0.317    | 0.584   |
| GdCl$_2$ | 45.95    | 13.53    | 1.028     | -1.906    | -0.878   | -2.708  |
| GdBr$_2$ | 40.46    | 11.68    | 0.847     | -1.742    | -0.895   | -3.110  |
| GdI$_2$  | 35.49    | 10.09    | 0.658     | -1.356    | -0.698   | -2.748  |

FIG. 9. (Color online) For monolayer GdCl$_2$, the elastic constants $C_{ij}$, the piezoelectric stress coefficient ($e_{11}$) along with the ionic contribution and electronic contribution, and the piezoelectric strain coefficient ($d_{11}$) with the application of biaxial strain (0.94 to 1.02).
have been predicted$^{19,20}$, and they possess in-plane magnetic anisotropy. Here, we use GGA+$U_{eff}$ ($U_{eff} = 5.0$ and $8.0$ eV for monolayer GdBr$_2$ and GdI$_2$, respectively) method to investigate piezoelectric properties of GdX$_2$ (X= Br and I) monolayers. The data related with elastic and piezoelectric properties are summarized in Table 1. It is found that $d_{11}$ of GdX$_2$ (X= Br and I) monolayers are comparable with one of GdCl$_2$.

VI. STRAIN EFFECTS

The VBM of unstrained monolayer GdCl$_2$ is at $\Gamma$ point, and it is necessary to tune VBM to $K$/-$K$ point by external field for practical applications. As is well known, the strain is a very effective method to tune the electronic structures of 2D materials$^{41-47}$. The $a/a_0$ is used to simulate the biaxial strain with $a$ and $a_0$ being the strained and unstrained lattice constants. In considered strain range, to confirm the FM ground state, the energy differences of AFM with respect to FM state vs $a/a_0$ with rectangle supercell are plotted in Figure 6. It is found the energy difference with the biaxial strain varying from 0.94 to 1.06 is always positive, and monotonically decreases. This indicates that the ground state of monolayer GdCl$_2$ is FM in considered strain range, and the strain can strengthen the FM coupling between Gd atoms from tensile strain to compressive one. At applied strain, it is also very important to confirm PMA for stable long-range magnetic ordering without external field. For MAE, Figure 6 shows a decrease with increasing $a/a_0$, and the MAE becomes negative value with the strain over 1.03, which means that the easy axis of monolayer GdCl$_2$ turns to in-plane.

We only show energy band structures of monolayer GdCl$_2$ (0.94 to 1.02) with PMA by using GGA+SOC in Figure 7, and the energy band gaps are plotted in Figure 6. At applied strain, monolayer GdCl$_2$ is always an indirect gap semiconductor. It is found that the compressive strain can induce the transition of VBM from $\Gamma$ point to $K$/-$K$ point, which can be observed at 0.98 strain. In fact, the change of VBM has been realized at only 0.99 strain, and the corresponding energy band is plotted in Figure 1 of electronic supplementary information (ESI). The tensile strain can make CBM change from M point to one point along $\Gamma$-M path. With $a/a_0$ from 0.94 to 1.02, the energy band gap firstly increases, and then decreases, which can be observed in many 2D materials$^{46,47}$. As shown in Figure 6, the valley splitting increases monotonically with the increasing $a/a_0$. Conversely, a compressive strain decreases the valley splitting, and the valley splitting will become negative value at about 0.963 strain, which implies that the energy of $-K$ valley is higher than one of $K$ valley. The Berry curvature distributions of monolayer GdCl$_2$ with $a/a_0$ being 0.94, 0.98 and 1.02 by using GGA+SOC are shown in Figure 8. It is found that the Berry curvatures (absolute value) of two valleys become large with increasing $a/a_0$.

It have been proved that strain engineering can effectively tune piezoelectric properties of 2D materials$^{48-51}$, and then we investigate the strain effects on piezoelectric properties of monolayer GdCl$_2$. The elastic constants ($C_{11}$, $C_{12}$ and $C_{11}$-$C_{12}$), piezoelectric stress coefficients ($e_{11}$) along the ionic and electronic contributions,
is found that the strain has little effects on $\varepsilon_{11}$, including both the ionic and electronic contributions. However, with increasing $a/a_0$, the $d_{11}$ (absolute value) increases due to reduced $C_{11}-C_{12}$ based on Equation 7.

Considering various factors, very small compressive strain (about 0.99 strain) can make monolayer GdCl$_2$ to be a good valley material with PMA, VBM at K/-K point, strong FM coupling, proper valley splitting and $d_{11}$ to realize PAVHE.

VII. ELECTRONIC CORRELATION EFFECTS

To further confirm the reliability of our results, the electronic correlation effects on magnetic, electronic and piezoelectric properties of monolayer GdCl$_2$ are investigated by choosing different $U$ (2-6 eV). The energy differences between AFM and FM states with rectangle supercell and MAE vs $U$ are plotted in Figure 10. With increasing $U$, the energy difference is always positive, and monotonically increases. These manifest that the monolayer GdCl$_2$ is always FM order, and the increasing $U$ can strengthen the FM coupling between Gd atoms. The MAE shows a decrease with decreasing $U$, and the MAE becomes negative value with easy axis turning to in-plane with $U$ being less than about 2.5 eV. The energy band structures of monolayer GdCl$_2$ ($U=2$ to 6 eV) by using GGA+SOC are plotted in FIG.2 of ESI, and the energy band gaps and valley splitting are plotted in Figure 10. When the $U$ increases, the VBM is always at K/-K point, and the gap increases. It is found that the electronic correlation has little influence on valley splitting, and the change only 1.2 meV with different $U$ (2-6 eV). From FIG.3 of ESI, the electronic correlation has little effects on Berry curvatures of K and -K valleys. The elastic constants ($C_{11}$, $C_{12}$ and $C_{11}-C_{12}$), piezoelectric stress coefficients ($\varepsilon_{11}$) along the ionic and electronic contributions, and piezoelectric strain coefficients ($d_{11}$) of monolayer GdCl$_2$ vs $U$ are shown in Figure 11. Calculated results show that electronic correlation has small effects on $d_{11}$ due to small influence on $C_{ij}$ and $\varepsilon_{11}$, and the change is about 0.21 pm/V.

VIII. DISCUSSION AND CONCLUSION

The GdX$_2$ (X=Cl, Br and I) monolayers have been predicted$^{19,20}$, and the easy axis of monolayer GdCl$_2$ is along the out of plane direction, while monolayer GdBr$_2$ and GdI$_2$ possess in-plane magnetic anisotropy. When the compressive strain is larger than 3%, the easy axis of monolayer GdBr$_2$ transfers from in-plane to out-of-plane$^{20}$. These mean that monolayer GdF$_2$ should have PMA due to small atomic radius of F atoms. For monolayer GdF$_2$, the energy difference between AFM and FM is 0.285 eV, which means that the FM order is the ground state. The optimized lattice constants is 3.465 Å, and the calculated $C_{11}$ and $C_{12}$ are 73.87 Nm$^{-1}$ and
The monolayer GdF₂ is dynamically stable due to missing imaginary frequency. The PMA of monolayer GdF₂ is confirmed, and the corresponding MAE is 137 μeV per Gd atom. The band structures of monolayer GdF₂ with SOC for magnetic moment of Gd along the positive z direction are plotted in Figure 12. The monolayer GdF₂ is a indirect gap semiconductor (0.80 eV) with VBM at K/-K point and CBM at Γ point. It is found that the energy of -K valley is higher than one of K valley with valley splitting of 47.6 meV. Calculated Berry curvature distribution of monolayer GdF₂ with SOC for magnetic moment of Gd along the positive z direction is plotted in FIG.5 of ESI. The absolute values of the Berry curvatures of K and -K valleys are smaller than ones of monolayer GdCl₂, and are no longer identical with the typical valley contrasting properties. Finally, the piezoelectric properties of monolayer GdF₂ are investigated, and the calculated $d_{11}$ is 0.584 pm/V. With respect to GdX₂ (X=Cl, Br and I) monolayers, the $d_{11}$ of monolayer GdF₂ becomes positive, which is because the electronic part of monolayer GdF₂ is larger than ionic one. The related data are summarized in Table I. These results show that monolayer GdF₂ may be a potential valley material to achieve PAVHE.

In summary, a possible way is proposed to achieve anomalous valley Hall effect by piezoelectric effect, and then the valleytronic and piezoelectric properties of monolayer GdCl₂ are investigated by the reliable first-principle calculations. Monolayer GdCl₂ is a FM semiconductor with a pair of valleys locating at the K and -K points, and possess PMA. Arising from the intrinsic magnetic interaction, broken inversion symmetry and SOC, the valley splitting can be observed between K and -K valleys, and the corresponding value is 42.3 meV. The predicted $d_{11}$ is -2.708 pm/V, which can provide a suitable in-plane electric field by uniaxial in-plane strain. Moreover, the effects of strain and electronic correlation on the valley physics and piezoelectric properties are also studied. Finally, a 2D FM semiconductor GdF₂ is predicted, which is also a potential ferrovalley material. Our work provides an initial idea for realizing and manipulating the valley physics.

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