Negative Piezoelectric Coefficient in Ferromagnetic 1H-LaBr₂ Monolayer

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Cite This: ACS Appl. Electron. Mater. 2022, 4, 850–855

ABSTRACT: The discovery of two-dimensional (2D) magnetic materials that have excellent piezoelectric response is promising for nanoscale multifunctional piezoelectric or spintronic devices. Piezoelectricity requires a noncentrosymmetric structure with an electronic band gap, whereas magnetism demands broken time-reversal symmetry. Most of the well-known 2D piezoelectrics, e.g., 1H-MoS₂ monolayer, are not magnetic. Being intrinsically magnetic, semiconducting 1H-LaBr₂ and 1H-VS₂ monolayers can combine magnetism and piezoelectricity. We compare piezoelectric properties of 1H-MoS₂, 1H-VS₂, and 1H-LaBr₂ using density functional theory. The ferromagnetic 1H-LaBr₂ and 1H-VS₂ monolayers display larger piezoelectric strain coefficients, namely, \( d_{11} = -4.527 \text{ pm/V} \) for 1H-LaBr₂ and \( d_{11} = 4.104 \text{ pm/V} \) for 1H-VS₂, compared to 1H-MoS₂ (\( d_{11} = 3.706 \text{ pm/V} \)). 1H-MoS₂ has a larger piezoelectric stress coefficient (\( e_{11} = 370.675 \text{ pC/m} \)) than 1H-LaBr₂ (\( e_{11} = -94.175 \text{ pC/m} \)) and 1H-VS₂ (\( e_{11} = 298.100 \text{ pC/m} \)). The large \( d_{11} \) for 1H-LaBr₂ originates from the low elastic constants, \( C_{11} = 30.338 \text{ N/m} \) and \( C_{12} = 9.534 \text{ N/m} \). The sign of the piezoelectric coefficients for 1H-LaBr₂ is negative, and this arises from the negative ionic contribution of \( e_{11} \), which dominates in 1H-LaBr₂ whereas the electronic part of \( e_{11} \) dominates in 1H-MoS₂ and 1H-VS₂. We explain the origin of this large ionic contribution of \( e_{11} \) for 1H-LaBr₂ through Born effective charges (\( Z_{ij} \)) and the sensitivity of the atomic positions to the strain (\( d\eta_j/d\eta_i \)). We observe a sign reversal in the \( Z_{ij} \) values of Mo and S compared to the nominal oxidation states, which makes both the electronic and ionic parts of \( e_{11} \) positive and results in the high value of \( e_{11} \). We also show that a change in magnetic order can enhance (reduce) the piezoresponse of 1H-LaBr₂ (1H-VS₂).

KEYWORDS: density functional theory (DFT), piezoelectric monolayer, 2D materials, 2D magnets, negative piezoelectric coefficient

INTRODUCTION

Piezoelectric materials are used in a wide range of important devices such as microphones, medical imaging, and sensors.\(^1,2\) Recently it has been demonstrated that the piezopotential originating from piezoelectricity can be used as a gate voltage to control the electronic band gap of a piezoelectric semiconductor, opening a new field of research named “piezotronics.”\(^1,2\) In this regard, 2D semiconductors are promising materials as they can sustain the large deformations present in piezoelectric applications.\(^1,2\) Moreover, these 2D materials show unique optical properties, for example, valleytronics.\(^3,4\) Hence, 2D materials can be ideal for piezophotonics where charges stemming from the piezoelectric effect can couple with light to significantly modulate the charge-carrier generation, separation, transport, and/or recombination in semiconducting nanostructures, promising better LEDs, photodetectors, and solar cells.\(^1,2\)

Piezoelectricity and valleytronics require broken inversion symmetry and a band gap. Promisingly, there already exists a wide range of noncentrosymmetric and intrinsically piezoelectric 2D materials.\(^3,4\) On the other hand, there are only a few 2D semiconductors/insulators to date in which both time-reversal and inversion symmetry are broken. These noncentrosymmetric magnetic 2D materials, e.g., vanadium dichalcogenide monolayers,\(^5\) exhibit spontaneous valley polarization, which can be controlled by a magnetic field.\(^5\) Very recently, the coexistence of magnetism and piezoelectricity has also been predicted in vanadium dichalcogenide monolayers.\(^5\) However, how the magnetic ordering impacts on their piezoelectricity remains unexplored. This understanding will allow us to couple magnetism and piezoelectricity for realizing multifunctional piezoelectric devices.

A piezoelectric stress coefficient (\( e_{ij} \)), defined as \( \frac{\partial P_j}{\partial \eta_i} \), where \( \partial P_j \) is the induced polarization along the \( i \)-direction in response to strain \( \partial \eta_j \) along the \( j \)-direction, can be split into two

Received: December 3, 2021
Accepted: January 6, 2022
Published: January 15, 2022
contributions: the ionic part, $\epsilon_{\text{ion}}^{ij}$, where ions are allowed to move under an applied strain, and the electronic part (also known as the clamped-ion part) $\epsilon_{\text{elc}}^{ij}$, where ions are clamped under applied strain. In many bulk materials, including wurtzite nitrides, $\epsilon_{\text{ion}}^{ij}$ is negative but is dominated by positive $\epsilon_{\text{elc}}^{ij}$, thus resulting in a positive value of $\epsilon_{\text{ij}}$. Generally, a positive longitudinal piezoelectric coefficient is expected as a tensile strain is expected to increase the induced electric polarization. However, very recently an anomalous negative piezoelectric coefficient has been observed in the layered ferroelectric CuInP$_2$S$_6$, although the coupling coefficient due to large negative $\epsilon_{\text{elc}}^{ij}$ has been observed in several hexagonal ABC ferroelectrics. A negative longitudinal piezoelectric coefficient would mean that the material contracts along the direction of an applied electric field rather than expands. This can enable novel nanoscale electromechanical devices, e.g., piezoelectric actuators.

This raises an interesting question: can a negative total $\epsilon_{\text{ij}}$ be obtained due to large negative $\epsilon_{\text{elc}}^{ij}$ instead of $\epsilon_{\text{ion}}^{ij}$? To answer this question, we investigate three intrinsically piezoelectric monolayers, 1H-MoS$_2$, 1H-VS$_2$, and 1H-LaBr$_2$, and we discover 1H-LaBr$_2$ as a new 2D piezoelectric monolayer that has a negative piezoelectric coefficient originating from a large negative $\epsilon_{\text{elc}}^{ij}$. Being a magnetic, semiconducting electride, 1H-LaBr$_2$ is a unique monolayer, although it has not been achieved experimentally yet; however, it is predicted to be feasible via chemical exfoliation from its layered bulk structure. It combines peculiar features; for example, its electron density shows neither complete localization at an atomic site nor metallic-like delocalization, but rather it occupies the center of the hexagon from which originate localized magnetic moments. Very recently, it has been predicted that this magnetism can be utilized for valley polarization. However, its piezoelectric properties have not been investigated to date.

Recently a number of 2D materials in the 1H structure ($D_{3h}$ symmetry) have been predicted to show large piezoelectric coefficients. These 2D materials still remain at the stage of fundamental research; understanding the origin of piezoelectricity can promote the discovery of more 2D piezoelectrics. Encouragingly, piezoelectricity has also been experimentally confirmed in the 1H-MoS$_2$ monolayer, and the value $\epsilon_{11} (2.9 \times 10^{-10} \text{ C/m})$ is in good agreement with first-principles calculations of $\epsilon_{11} = 3.64 \times 10^{-10} \text{ C/m}$. Recently, the coexistence of magnetism and piezoelectricity has also been predicted in the 1H-VS$_2$ monolayer, although the coupling between magnetic order and piezoelectricity was not discussed. Note that research on these 1H structured 2D piezoelectrics is mainly devoted to finding large piezoelectric coefficients, overlooking their sign as they generally show positive in-plane piezoelectric coefficients.

However, the origin of the piezoelectric co-coefficients in both magnitude and sign still remains unclear. Questions include the following: Why is the $\epsilon_{11}$ of the 1H-MoS$_2$ monolayer larger than that of the 1H-VS$_2$ monolayer? Why is the sign of the ionic part of $\epsilon_{11}$ positive in the 1H-MoS$_2$ monolayer but negative in the 1H-VS$_2$ monolayer? In this paper, we show that the answers to these questions have their origin in the Born effective charges (BECs), the sensitivity of the atomic positions in response to a strain ($\frac{\partial u_i}{\partial \epsilon_{ij}}$), and the bond strength. We also demonstrate that the 1H-LaBr$_2$ monolayer can be a magnetic, piezoelectric material. Moreover, we show that antiferromagnetic ordering makes the isotropic piezoelectricity of the ferromagnetic 1H-LaBr$_2$ monolayer anisotropic (i.e., $\epsilon_{11} \neq -\epsilon_{12}$).

### COMPUTATIONAL DETAILS

Our first-principles calculations are performed in the framework of spin-polarized density functional theory using projector augmented wave (PAW) potentials to describe the core electrons and the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) for exchange and correlation as implemented in the Vienna Ab initio Simulation Package (VASP) based on a plane-wave basis set. The valence electron configurations for La, V, Mo, S, and Br are 4$p^5$5$s^2$6$d^1$ (nine electrons), 3$p^3$4$d^3$5$s^1$ (11 electrons), 4$p^4$4$d^5$5$s^1$ (12 electrons), 3$s^2$3$p^1$ (six electrons), and 4$s^4$4$p^3$ (seven electrons), respectively. A cutoff energy of 500 eV for the plane-wave expansion is used in all calculations, and all structures are fully relaxed until the Hellmann–Feynman forces on all the atoms are less than $10^{-3}$ eV/Å. An effective onsite Coulomb interaction parameter ($U_{\text{eff}}$) of 6.5 eV is used for the La f-electrons. The lattice parameters and internal coordinates of the 2D structures are fully relaxed to achieve the lowest energy configuration using the conjugate gradient algorithm. To prevent the interaction between the periodic images in the calculations, a vacuum layer with a thickness of approximately 25 Å is added along the z-direction (perpendicular to the monolayer) in the supercell. Note that a rectangular cell (see Figure 1) is used instead of a primitive hexagonal one for applying strain along the desired direction. This is a commonly used approach.

Geometry optimization is carried out employing the conjugated gradient technique, and the convergence for the total energy is set as $10^{-7}$ eV. The Brillouin zone integration is sampled using a regular $6 \times 8 \times 1$ Monkhorst–Pack k-point grid, for geometry optimizations, while a denser grid of $12 \times 16 \times 1$ is used for density functional perturbation theory (DFPT) calculations. The elastic stiffness coefficients ($C_{ij}$) are obtained with a finite difference method as implemented in the VASP code. DFPT as implemented in the VASP code is used to calculate Born effective charges ($Z_{ij}$) and ionic and electronic parts of piezoelectric ($\epsilon_{ij}$) tensors.

### RESULTS AND DISCUSSION

Table 1 shows the lattice parameters of the monolayers. We use a rectangular unit cell, and lattice parameter $a$ should be equal to $b \sqrt{3}$ for an ideal 1H structure. Our calculated lattice parameters are in good agreement with previously reported values.
1H-LaBr₂ has significantly larger lattice parameters compared to these of the other two monolayers—mainly because the ionic radius of La (Br) is larger than that of Mo/V (S) according to the Database of Ionic Radii (http://abulafile.mtc.ac.uk/shannon/ptable.php). However, we notice that strip antiferromagnetic (AFM) ordered structures shown in Figure 1 deviate from the ideal relationship, shrinking along the zigzag, or b-axis, direction and expanding along the armchair, or a-axis, direction. We quantify this deviation as

\[
\left( \frac{a - b \sqrt{3}}{b \sqrt{3}} \right) \times 100\%
\]

This is about 1.22% (0.72%) for the AFM 1H-LaBr₂ (1H-VS₂) monolayer. This deviation is also reflected in the change in angles θ₁₁ and θ₂₂, which are defined in Figure 1.

In agreement with previous reports,⁶,⁷,⁶¹-⁶⁴,11 we find that ferromagnetic (FM) ordering is the ground state for both 1H-LaBr₂ and 1H-VS₂ monolayers, lying 51.520 and 88.545 meV lower in energy compared to the strip AFM state. However, the magnetic order of these monolayers has not been clearly identified in experiments to date. Although the VS₂ monolayer has not yet been synthesized, ferromagnetism has been recently found in its ultrathin films.²²,²³

The 1H-LaBr₂(FM), 1H-VS₂(FM), and 1H-MoS₂ monolayers belong to the nonmagnetic space group P6/m2 (157), that is, considering their structures but without their magnetic order. Unlike the corresponding bulk materials, this structure has no inversion symmetry and is intrinsically piezoelectric. We calculated their piezoelectric stress coefficients, which are shown in Table 2. The piezoelectric coefficients that involve strain along the z-direction are ill-defined for the monolayers. Our 1H monolayers have only one independent piezoelectric coefficient, ε₁₁ (ε₁₂ = −ε₁₂), due to 6/m2 point group symmetry. Table 2 shows that 1H-MoS₂ has a quite large ε₁₁ value compared to those of the other two monolayers. Interestingly, FM 1H-LaBr₂ shows a negative ε₁₁, which is also quite low compared to those of the other materials. To understand the origin of piezoelectric constant, ε₁₁ and ε₁₂ can be decomposed into two parts:²⁴

\[
e_{11} = e^{\text{elc}}_{11} + \sum_k e^{\text{ion}}_{11}(k) = e^{\text{elc}}_{11} + \sum_k \frac{\varepsilon a^2}{A} Z_{11}(k) \frac{d\mu(k)}{d\eta_i}
\]

(1)

\[
e_{12} = e^{\text{elc}}_{12} + \sum_k e^{\text{ion}}_{12}(k) = e^{\text{elc}}_{12} + \sum_k \frac{\varepsilon a^2}{A} Z_{12}(k) \frac{d\mu(k)}{d\eta_2}
\]

(2)

The clamped-ion term (e^{\text{elc}}_{11} or e^{\text{elc}}_{12}) arises from the contributions of electrons when the ions are frozen at their zero-strain equilibrium internal atomic coordinates (u), and the internal-strain (e^{\text{ion}}_{11} or e^{\text{ion}}_{12}) term arises from the contribution from internal microscopic atomic displacements in response to a macroscopic strain. In our case, the strain (η) is applied in the x-direction (see Figure 1). Here, k runs over all the atoms in the unit cell. a is the in-plane lattice constant, ε is the electron charge, and A is the area as the 2D unit is used. The Born effective charge (Z₁₁(η)) of the kth atom is calculated by the DFPT approach. The response of the kth atom’s internal coordinate along the x-direction (u₁(k)) in response to a macroscopic strain (η) is measured by dμ(k)/dη. Table 2 shows that both e^{\text{elc}}_{11} and e^{\text{ion}}_{11} have the same sign—positive—for 1H-MoS₂, unlike the other two monolayers. This results in a large total ε₁₁ for 1H-MoS₂. Note that other 1H-MX₂ (M = Mo, W, Cr and X = S, Se, Te) monolayers also exhibit positive ε₁₁ and ε₁₂ (see Table S1).³⁻⁸ However, due to the opposite signs of ε₁₁ and ε₁₂ in 1H-VS₂(FM), its total ε₁₁ is smaller than the ε₁₁ for 1H-MoS₂, even though it has a larger value of ε₁₂ (see Table 2). Interestingly, 1H-LaBr₂(FM) shows a negative ε₁₁, which is significantly larger than its ε₁₁, thus resulting in a negative total ε₁₁. This is different from the recently discovered negative piezoelectric coefficient in layered ferroelectrics and wurtzite, where the negative sign comes from ε₁₁.⁷ Here it is important to highlight that other 2D piezoelectrics, e.g., the well-known hexagonal boron nitride (h-BN) monolayer⁷ and the 1H-VSe₂ monolayer,¹¹ have negative ε₁₁ values but the ε₁₁ part dominates, resulting in positive ε₁₁. Interestingly, we find that h-AlN and h-ZnO monolayers also exhibit negative ε₁₁ values due to large negative ε₁₁ values (see Table S1). We hope that our finding will inspire experimental studies of negative in-plane piezoresistance (ε₁₁) in 2D materials. Deepening our understanding about the 2D piezoelectrics, this would enable discovery of 2D materials for novel electromechanical applications.

Table 2. Electronic (e^{\text{elc}}_{11}) and Ionic (e^{\text{ion}}_{11}) Parts of the Total Piezoelectric Stress Constant ε₁₁ and Born Effective Charge Z₁₁

| Monolayer        | ε₁₁  | ε₁₂  | ε₁₁  | Z₁₁(M) | Z₁₁(X) | dμ/μ(dη₁) | dμ/μ(dη₂) |
|------------------|------|------|------|--------|--------|----------|----------|
| 1H-MoS₂          | 315.000 | 56.050 | 371.050 | −1.006  | 0.503  | −0.037   | 0.018    |
| 1H-VS₂(FM)³⁻⁸    | 739.025 | −80.925 | 298.100 | 1.359   | −0.680 | −0.038   | 0.021    |
| 1H-LaBr₂(FM)⁷⁻¹¹ | 111.175 | −205.350 | −94.175 | 2.540   | −1.269 | −0.069   | 0.035    |

"In 2D piezoelectric unit, pC/m. M = Mo, V, and La and X = S and Br in lel, where ε is the charge of an electron. "Here, dμ/μ(η) represents the change of the position of the atoms along the a-direction under a strain along the a-direction (η₁). "Both 1H-VS₂ and 1H-LaBr₂ monolayers are in the ferromagnetic (FM) state."
Now to understand the origin of negative/positive $\epsilon^{\text{ion}}_{\text{i}l}$, we expressed $\epsilon^{\text{ion}}_{\text{i}l}$ in terms of $Z_{\text{i}l}$ and $d_{\text{u}l}(k)$ (see eq 1). Providing microscopic insight into the piezoelectric coefficients, BEC is a dynamical charge that is directly related to the change of electric polarization or dipole moment (for molecules) in response to an atomic displacement.$^{25}$ $Z_{\text{i}l}(k)$ is proportional to $\frac{\partial \rho_{\text{i}l}(k)}{\partial k}$, where $\partial \rho_{\text{i}l}$ is the change of the dipole moment in the x-direction induced by a small displacement of atom $k$ in the same direction ($\partial r_{\text{i}}(k)$).$^{25}$ The negative slope $\left(\frac{\partial \rho_{\text{i}l}(k)}{\partial k}\right)$ will result in a negative BEC, which is the case for 1H-MoS$_2$. This proportionality (i.e., the slope) is the origin of BECs and has the dimensionality of an electric charge. This charge is a well-defined and experimentally measurable quantity—owing to the fact that the BECs are related to $\text{LO}$-$\text{TO}$ splitting, which is the frequency difference between the longitudinal (LO) and transverse (TO) optical phonon modes.$^{25}$ From Table 2, it is clear that the positive $\epsilon^{\text{ion}}_{11}$ in 1H-MoS$_2$ is due to unusual BECs of Mo and S as we see a negative (positive) sign for cation Mo (anion S) in the BECs. Such counterintuitive BECs—Mo (S) shows a negative (positive) dynamical charge, opposite to its static positive charge—are also reported for bulk 2H-MoS$_2$.$^{26}$ Interestingly, we notice that other good 2D piezoelectric transition metal (Mo, W, and Cr) dichalcogenide (S, Se, and Te) monolayers also exhibit counterintuitive BECs—Mo (S) shows a negative (positive) dynamical charge, opposite to its static positive charge—are also reported for bulk 2H-MoS$_2$.$^{26}$ Additionally, such counterintuitive BECs—Mo (S) shows a negative (positive) dynamical charge, opposite to its static positive charge—are also reported for bulk 2H-MoS$_2$.$^{26}$

The origin of the negative sign in $\epsilon^{\text{ion}}_{11}$ of 1H-MoS$_2$ is in its $\text{Mo-S}$ distance of 2.417 Å, or V$_{12}$ for FM. Moreover, $\epsilon^{\text{ion}}_{11}$ of 1H-LaBr$_2$(FM) is about 22% larger than that of the well-known 2D piezoelectric 1H-MoS$_2$ because the former has quite low elastic constants.$^{18}$

### Table 3. Elastic Constants ($C_{11}$ and $C_{12}$), ICOHP of a Bond between Cation (Mo/V/La) and Anion (S/Br), Poisson’s ratio $\nu$ ($=C_{12}/C_{11}$), and Piezoelectric Stress Coefficient $d_{11}$

|       | $C_{11}$ (N/m) | $C_{12}$ (N/m) | ICOHP (eV/bond) | $\nu$ | $d_{11}$ (pm/V) |
|-------|---------------|---------------|----------------|------|---------------|
| 1H-MoS$_2$ | 133,214       | 33,105        | $-3.113$       | 0.249 | 3.706         |
| 1H-VS$_2$(FM) | 101,421     | 28,785        | $-2.510$       | 0.284 | 4.104         |
| 1H-LaBr$_2$(FM) | 30,338       | 9,534         | $-1.919$       | 0.314 | $-4.527$      |

Now we discuss how the magnetic ordering can affect the piezoelectric response. We consider simple strip-type antiferromagnetic (AFM) order (see Figure 1). The calculated values of $\epsilon_{11}$ and $\epsilon_{12}$ are shown in Table 4. Interestingly, we find that $\epsilon_{11}$ is not equal to $-\epsilon_{12}$ for AFM, whereas $\epsilon_{11} = -\epsilon_{12}$ for FM. Moreover, $\epsilon_{11}$ in AFM is quite different from $\epsilon_{11}$ in FM (see Table 4). For example, $\epsilon_{11}$ of AFM 1H-LaBr$_2$ is almost double compared to that of FM; however, $\epsilon_{11}$ is still negative. To understand the origin of $\epsilon_{11}$, we consider two cases: (i) the structures (lattice parameters $a$ and $b$ and atomic positions) are relaxed and (ii) AFM order is used, keeping the lattice parameters $a$ and $b$ and atomic positions fixed in their FM structures, which are represented by asterisks in Table 4.

Now we calculate the piezoelectric stress constants ($d_{ij}$) using $\epsilon_{ij}$ and elastic constants ($C_{ij}$) (see Table 3). First, the mechanical/elastic stability of the ferromagnetic (FM) 1H-LaBr$_2$, monolayer is checked according to the criteria for a 2D hexagonal crystal structure: $C_{11} > C_{12}$ and $C_{66} > 0$. Considering the two independent elastic constants (only two independent elastic constants due to space group $P6_3m2$ and two-dimensionality) that we obtain, namely, $C_{11} = 30.34$ N/m and $C_{66} = 9.53$ N/m (notice that $C_{66} = (C_{11} - C_{12})/2$), it can be concluded that the monolayer is mechanically stable. The dynamic stability of 1H-LaBr$_2$ in terms of phonon modes has already predicted.$^{10}$ Our calculated elastic coefficients for the monolayers are in good agreement with the previously reported values.$^{6,10,18}$ Compared to 1H-MoS$_2$ and 1H-VS$_2$(FM) monolayers, its lower $C_{11}$ and $C_{12}$ values but larger $\nu$ indicate that the 1H-LaBr$_2$(FM) monolayer is much softer. This is also expected because of its larger lattice parameters. This softening of elastic coefficients can also be understood from bond strength analysis. For that, we use the ICOHP approach,$^{28}$ which allows us to quantify the strength of the covalency of a bond. The more negative ICOHP, the stronger the covalent bonding. Here we emphasize that ICOHP is a reasonable qualitative estimation of the bond strength but it is not the bond enthalpy. We see in Table 3 that the 1H-LaBr$_2$(FM) monolayer has a significantly weaker La–Br bond, with an ICOHP of $-1.919$ and a La–Br bond length of 3.14 Å, compared to those of Mo–S, with an ICOHP of $-3.113$ and a Mo–S distance of 2.417 Å, or V–S, with an ICOHP of $-2.510$ and a V–S distance of 2.366 Å. Table 3 shows that $d_{11}$ (again the only independent coefficient due to symmetry and dimensionality; $d_{11} = \frac{1}{2}(\epsilon_{11} + \epsilon_{12})$) of 1H-LaBr$_2$(FM) is about 22% larger than that of the well-known 2D piezoelectric 1H-MoS$_2$ because the former has quite low elastic constants. The origin of the negative sign in $d_{11}$ of 1H-LaBr$_2$(FM) is in its negative $\epsilon_{11}$, which is discussed above. As also previously reported,$^{18}$ despite being ultrathin, the piezoelectric coefficients of these 2D piezoelectrics are comparable with those of well-known bulk piezoelectrics, e.g., $\alpha$-quartz ($d_{11} = 2.3$ pm/V)$^{29}$ and wurtzite nitrides such as AlN ($d_{33} = 5.1$ pm/V)$^{10}$ and GaN ($d_{33} = 3.1$ pm/V)$^{10}$. The crystal orbital Hamilton population (ICOHP). In addition, compared to the other two monolayers, its larger lattice parameters (see Table 1) can promote larger displacement of atoms in response to strain as atoms have more space to move. We propose that BECs and lattice parameters—rather than static charges like Bader charge—can be ideal descriptors for searching for improved 2D piezoelectrics as they are directly related to the $\epsilon_{ij}$ and can be routinely computed, allowing for automated and high-throughput screening. Our results also explain the previous observation that there is no significant correlation of $d_{11}$ with electronegativity or Bader charges, whereas $d_{11}$ shows a strong correlation with polarizabilities of anions and cations.$^{13}$ Note that BECs can also be considered as a manifestation of local polarizabilities of atoms.$^{25}$
Table 4. Electronic ($\epsilon^{el}_{ij}$ and $\epsilon^{el}_{11}$) and Ionic ($\epsilon^{ion}_{11}$ and $\epsilon^{ion}_{12}$) Parts of the Total Piezoelectric Stress Constants $\epsilon_{11}$ and $\epsilon_{12}$ of Antiferromagnetic 1H-VS$_2$ and 1H-LaBr$_2$ Monolayers$^*$ and Born Effective Charge $Z_{11}^{BEC}$

|       | $\epsilon^{el}_{11}$ | $\epsilon^{ion}_{11}$ | $\epsilon_{11}$ | $Z_{11}(M)$ | $Z_{11}(X)$ | $d_{11}(M)$ | $d_{11}(X)$ | $d_{12}(M)$ | $d_{12}(X)$ |
|-------|----------------------|-----------------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| 1H-VS$_2$ | 221.000              | $-$38.375             | 183.525         | 0.662       | $-$0.210    | $-$0.031    | 0.015       | $-$284.150  | 12.175      | $-$271.975  | 0.025       | $-$0.013    |
| 1H-VS$_2^{AFM}$ | 218.075              | $-$14.525             | 203.550         | 0.657       | $-$0.203    | $-$0.033    | 0.016       | $-$280.825  | 40.200      | $-$240.625  | 0.026       | $-$0.013    |
| 1H-LaBr$_2$ | 43.650               | $-$269.025            | $-$225.375      | 2.765       | $-$1.381    | $-$0.079    | 0.040       | $-$96.225   | 199.300     | 103.075     | 0.066       | $-$0.033    |
| 1H-LaBr$_2^{AFM}$ | 57.275               | $-$281.000            | $-$223.725      | 2.744       | $-$1.370    | $-$0.083    | 0.041       | $-$100.075  | 197.700     | 97.625      | 0.068       | $-$0.034    |

$^*$In 2D piezoelectric unit, pC/m. $^\text{4}$M = Mo, V, and La and X = S and Br in lel, where $\epsilon$ is the charge of an electron. Here, $\frac{d_{11}}{d_{12}}$ represents the change of the position of the atoms along the $a$-direction under a strain along the $b$-direction ($\eta_b$). $^\text{5}$1H-VS$_2$ and 1H-LaBr$_2$ represent antiferromagnetic 1H-VS$_2$ and 1H-LaBr$_2$ monolayers in their ferromagnetic structures (i.e., just the magnetic order is changed, no structural relaxation).

Table 5. Elastic Constants ($C_{11}$, $C_{22}$, and $C_{12}$) and Piezoelectric Strain Coefficients ($d_{11}$ and $d_{12}$)

|       | $C_{11}$ (N/m) | $C_{22}$ (N/m) | $C_{12}$ (N/m) | $d_{11}$ (pm/V) | $d_{12}$ (pm/V) |
|-------|---------------|---------------|---------------|-----------------|-----------------|
| 1H-VS$_2$(AFM) | 94.586        | 105.378       | 32.867        | 2.832           | $-$3.359        |
| 1H-LaBr$_2$(AFM) | 28.005        | 31.198        | 8.981         | $-$10.343       | 6.137           |

change, resulting in changes to $\epsilon^{ion}$. We notice that the magnitude of $Z_{11}$ for both La (V) and Br (S) in AFM order has increased (decreased), promoting enhancement in total $\epsilon_{11}$ or $\epsilon_{12}$.

We also calculate the $d_{ij}$ coefficients (see Table 5) using the relation

$$d_{ij} = \sum_{k=1}^{6} \epsilon_{ik}(C^{-1})_{kj}$$

We notice that $C_{11}$ is not equal to $C_{22}$ for AFM structures. As $\epsilon_{11} \neq -\epsilon_{22}$ and $C_{11} \neq -C_{22}$ for AFM structures, $d_{11} \neq -d_{12}$ for AFM as shown in Table 5 is expected. We find that the $d_{11}$ (also $\epsilon_{11}$) of AFM 1H-LaBr$_2$ is about 2 times larger than that of its FM. We believe that such a change in piezoresistance induced by magnetic order can also be observed in other magnetic 2D piezoelectrics. In experiments, the magnetic direction (noncollinear magnetic order) can play a vital role, which is beyond the scope of this paper. Note that changing the magnetic order in a controlled way experimentally might be a challenge—especially for the change from FM to AFM. However, a transition from the AFM state to the FM state can be achieved by applying an external magnetic field to the AFM ordered samples.

**CONCLUSION**

We show that the 1H-LaBr$_2$ monolayer exhibits an unusual in-plane negative piezoelectric coefficient, unlike many other 1H structured 2D piezoelectrics. This would mean that the monolayer contracts along the $x$-direction (armchair direction) rather than expands, when an electric field is applied in the $x$-direction. Here the origin of the negative piezoelectric coefficient is because of a large negative $\epsilon^{ion}_{11}$ that cannot be compensated by $\epsilon^{el}_{11}$, this is different from hitherto observed negative piezoelectric coefficients in some bulk materials due to large $\epsilon^{el}_{ij}$ values. The 1H-LaBr$_2$ monolayer is a promising 2D piezoelectric, having a large piezoelectric $d_{11}$ ($-4.527$ pm/V) coefficient, which is comparable to those of well-known 2D piezoelectric 1H-Mo$_2$S$_3$ and 1H-VS$_2$ monolayers and is larger than that of bulk wurtzite GaN ($d_{11} \sim 3.1$ pm/V). We also explain the origin—both sign and magnitude—of the piezoelectric coefficients of three monolayers (1H-LaBr$_2$, 1H-Mo$_2$S$_3$, and 1H-VS$_2$) in terms of their dynamical charges (BECs) and atomic sensitivity ($\frac{\partial u}{\partial \eta}$) to an applied strain. Being directly linked with $\epsilon_{ij}$, we propose that BECs, rather than a static charge like the Bader charge, which relate to atom polarizability, can be good descriptors for searching new 2D piezoelectrics, also providing insight into the underlying mechanism. The calculation of BECs can be automated to allow for high-throughput screening. Additionally, we show that a change in magnetic order can have an effect on their piezoresponse quite significantly, which can be a unique way for coupling magnetism and electromechanical properties in 2D magnets.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaelm.1c01214.

Electronic ($\epsilon^{el}_{ij}$) and ionic ($\epsilon^{ion}_{11}$) parts of total piezoelectric stress constant $\epsilon_{11}$; Born effective charge $Z_{11}$ and $d_{11}/\partial \eta_1$ of 1H-MoS$_2$, 1H-MoSe$_2$, 1H-MoTe$_2$, 1H-WS$_2$, 1H-WSe$_2$, 1H-WTe$_2$, 1H-Cr$_2$, 1H-Cr$_2$Se$_2$, 1H-Cr$_2$Te$_2$, h-BN, h-AlN, and h-ZnO (PDF).

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This publication has emanated from research conducted with the financial support of Science Foundation Ireland (SFI) under Grant No. 20/EP/3710. The calculations were performed with the high-performance computing facilities of the Tyndall National Institute. The authors also acknowledge access to

854 https://doi.org/10.1021/acsaelm.1c01214
ACS Appl. Electron. Mater. 2022, 4, 850–855

ACS Applied Electronic Materials
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Issue 2022"
computing resources at Irish Centre for High-End Computing (ICHEC).

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