Ferromagnetic 1H-LaBr$_2$ monolayer: a promising 2D piezoelectric

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The discovery of two dimensional (2D) materials that have excellent piezoelectric response along with intrinsic magnetism is promising for nanoscale multifunctional piezoelectric or spintronic devices. Piezoelectricity requires non-centrosymmetric structures with an electric band-gap, whereas magnetism demands broken time-reversal symmetry. Most of the well-known 2D piezoelectric materials – e.g., 1H-MoS$_2$ monolayer – are not magnetic. Being intrinsically magnetic, semiconducting 1H-LaBr$_2$ and 1H-VS$_2$ monolayers can combine magnetism and piezoelectricity. We compare piezoelectric properties of 1H-MoS$_2$, 1H-VS$_2$ and 1H-LaBr$_2$ using density functional theory. Our results show that ferromagnetic 1H-LaBr$_2$ 2D monolayer displays a larger piezoelectric strain co-efficient ($d_{11} = -4.532$ pm/V, which is close to $d_{11} = -4.104$ pm/V of 1H-VS$_2$ monolayer) compared to that of well-known 1H-MoS$_2$ monolayer ($d_{11} = -3.706$ pm/V), while 1H-MoS$_2$ monolayer has a larger piezoelectric stress co-efficient ($e_{11} = -370.675$ pC/m) than the 1H-LaBr$_2$ monolayer ($e_{11} = -94.175$ pC/m, which is also lower than $e_{11} = 298.100$ pC/m of 1H-VS$_2$ monolayer). These in-plane piezoelectric $d_{11}$ coefficients are quite comparable with piezo-response of bulk wurzite nitrdes e.g., $d_{33}$ of GaN is about 3.1 pm/V. The large $d_{11}$ for 1H-LaBr$_2$ monolayer originates from the low elastic constants, $C_{11} = 30.338$ N/m and $C_{12} = 9.534$ N/m. Interestingly, the sign of the piezoelectric co-coefficients for 1H-LaBr$_2$ monolayer is different to that of the 1H-MoS$_2$ or 1H-VS$_2$ monolayers. The negative sign arises from the negative ionic contribution of $e_{11}$, which dominates in the 1H-LaBr$_2$ monolayer, whereas the electronic part of $e_{11}$ dominates in 1H-MoS$_2$ and 1H-VS$_2$. Furthermore, we explain the origin of this large ionic contribution of $e_{11}$ for 1H-LaBr$_2$ in terms of the Born effective charges ($Z_{ij}$) and the sensitivity of the atomic positions to the strain ($\frac{\partial a_{ij}}{\partial b_{ij}}$). Surprisingly, we observe a sign reversal in the $Z_{11}$ 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 $e_{11}$. Additionally, our interatomic bond analysis using crystal orbital Hamilton populations indicates that the weaker covalent bond in 1H-LaBr$_2$ monolayer is responsible for large $\frac{\partial a_{ij}}{\partial b_{ij}}$ and elastic softening (lower elastic constants).

I. INTRODUCTION

Piezoelectric materials are used in 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 a large deformation[1][2]. Moreover, these 2D materials show unique optical properties, for example valleytronics[3][4]. Hence, 2D materials can be ideal for piezo-photonics 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 nano-structures, promising better LED, photodetector, and solar cell[1][2].

Piezoelectricity and valleytronics require broken inversion symmetry and a band gap. Promisingly there already exists a wide range of non-centrosymmetric 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. Very recently, the co-existence of magnetism and piezoelectricity has 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 co-efficient ($e_{ij}$) – is defined as $\frac{\partial P_i}{\partial b_{ij}}$, where $\partial P_i$ is the induced polarization along $i$-direction in response to strain $\partial b_{ij}$ along $j$-direction – can be split into two contributions – ionic part $e_{ij}^{elc}$, where ions are allowed to move under an applied strain and electronic part (also known as clamped-ion part) $e_{ij}^{elc}$, where ions are clamped under a strain. In many bulk materials, including wurzite nitrdes[6][7], $e_{ij}^{elc}$ is negative but is dominated by $e_{ij}^{ion}$, thus resulting in a positive value of $e_{ij}$. 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 co-efficient has been observed in the layered ferroelectric CuInP$_2$S$_6$[8], which is explained in terms of its large negative $e_{ij}^{elc}$ that is not overcome by positive $e_{ij}^{ion}$. Also, negative piezoelectric coefficients – due to their large negative $e_{ij}^{elc}$ – have been observed in several hexagonal ABC ferroelectrics[8]. This raises an interesting question: can a negative total $e_{ij}$ be obtained due to large negative $e_{ij}^{ion}$? 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 co-efficient originating from a large negative $e_{ij}^{elc}$. 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[2]. It combines peculiar features – for example, its electron density shows neither complete localization at an atomic site nor metal-like delocalization, rather occupies at the center of the hexagon that originates localized magnetic moments[10][11]. Very recently, it has been predicted that this magnetism can be utilized for valley polarization[9]. However, its piezoelectric properties have not been investigated to date.

Recently a number of 2D materials in the 1H structure (D3h symmetry) have been predicted to show large piezoelectric co-efficients [12-15]. These 2D materials still remain at the stage of fundamental research, understanding the origin of piezoelectricity can promote discovery of more 2D piezoelectrics. Encouragingly, piezoelectricity has also been experimentally confirmed in 1H-MoS2 monolayer[16], and the value e11 (2.9x10^{-10} C/m) is in good agreement with first-principles calculations, e11 = 3.64x10^{-10} C/m[17]. Recently, coexistence of magnetism and piezoelectricity has also been predicted in 1H-VS2 monolayer[9], although the coupling between magnetic order and piezoelectricity was not discussed. Note that research on these 1H structured 2D piezoelectrics is mainly devoted to find large piezoelectric coefficients, overlooking their sign as they generally show positive in-plane piezoelectric coefficients[9, 12-15, 17]. However, the sign of the piezoelectric coefficients in both magnitude and sign still remains unclear. Questions include: why is the e11 of 1H-MoS2 monolayer larger than that of 1H-VS2 monolayer? Why is the sign of the ionic part of e11 in 1H-MoS2 monolayer positive, but negative in 1H-VS2 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 (\(\frac{dn}{dz}\)), and the bond strength. We also demonstrate that the 1H-LaBr3 monolayer[9][11] can be a magnetic, piezoelectric material. Moreover, we show that antiferromagnetic ordering makes the isotropic piezoelectricity of ferromagnetic 1H-LaBr3 monolayer anisotropic (i.e., e11 ≠ −e12).

II. 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) [18-20] based on a plane-wave basis set. The valence electron configurations for La, V, Mo, S, Br are 4p6 5s2 6d1 (9 electrons), 3p6 3d4 4s1 (11 electrons), 4p6 4d5 5s1 (12 electrons), 3s2 3p1 (6 electrons), 4s2 4p1 (7 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 on-site coulomb interaction parameter (Ueff) of 6.5 eV is used for the La f-electrons[10]. The lattice parameters and internal coordinates of the 2D structures are fully relaxed to achieve the lowest energy configuration using 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 primitive hexagonal one for applying strain along the desired direction. This is a commonly used approach[5][17]. 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 × 8 × 1 Monkhorst-Pack k-point grid, for geometry optimizations, while a denser grid of 12 × 16 × 1 is used for density functional perturbation theory (DFPT) calculations. The elastic stiffness coefficients (C_{ij}) are obtained using a finite difference method as implemented in the VASP code. DFPT is used to calculate Born effective charges (Z_{ij}) and ionic and electronic parts of piezoelectric (e_{ij}) tensors.

III. 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[5, 9][11][17]. 1H-LaBr3 has significantly larger lattice parameters, compared to those of other two monolayers – mainly because ionic radius of La (Br) is larger than that of Mo/V(S) according to database http://abulafia.mp.ri.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 (b-axis)
Table I. Structural information of the monolayers: optimized lattice parameters (a and b; see the rectangular cell in Fig 1) and the angle $\angle \text{Mo}/\text{V}/\text{La}/\text{S}/\text{Br}/\text{Mo}/\text{V}/\text{La}$. $\theta_{\text{FM}}$ and $\theta_{\text{AFM}}$ are the angles $\angle V_{\uparrow}/\text{La}/S/\text{Br}/V_{\uparrow}/\text{La}$ and $\angle V_{\uparrow}/\text{La}/S/\text{Br}/V_{\downarrow}/\text{La}$, where $\uparrow$ or $\downarrow$ arrows represent up or down spin polarization. The angle $\angle \text{Mo}/\text{S}/\text{Mo}$ is 82.537°.

|       | a (Å) | b (Å) | $\theta_{\text{FM}}$ | $\theta_{\text{AFM}}$ |
|-------|-------|-------|----------------------|----------------------|
| 1H-MoS$_2$ | 5.522 | 3.188 | -                    | -                    |
| 1H-VS$_2$(FM) | 5.504 | 3.178 | 84.372°              | -                    |
| 1H-VS$_2$(AFM) | 5.502 | 3.154 | 84.177°              | 84.518°              |
| 1H-LaBr$_2$(FM) | 7.298 | 4.214 | 84.189°              | -                    |
| 1H-LaBr$_2$(AFM) | 7.344 | 4.189 | 83.624°              | 84.556°              |

direction and expanding along the armchair (a-axis) direction. We quantify this deviation as $\frac{(a-b)/3}{a} \times 100\%$. This is about 1.22% (0.72%) for AFM 1H-LaBr$_2$ (1H-VS$_2$) monolayer. This deviation is also reflected in the change in angles $\theta_{\text{FM}}$ and $\theta_{\text{AFM}}$ (see Figure 1).

In agreement with previous reports[3, 9, 11], we find that ferromagnetic (FM) ordering is the ground state for both 1H-LaBr$_2$ and 1H-VS$_2$ monolayers, lying 51.520 meV and 88.545 meV lower in energy compared to strip AFM state. However, the magnetic order of these monolayers has not been clearly identified in experiments to date. Although VS$_2$ monolayer has not yet been synthesized, ferromagnetism has been recently found in its ultra-thin films[23, 24].

1H-LaBr$_2$(FM) and 1H-VS$_2$(FM) monolayers belong to non-magnetic (i.e., just considering their structure but without considering their magnetic order) space group P6m2 (157), the same as 1H-MoS$_2$. 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 z-direction are ill-defined for the monolayers. Our 1H monolayers have only one independent piezoelectric coefficient $e_{11}$ (note that $e_{11} = -e_{12}$) due to 6m2 point group symmetry. Table 2 shows that 1H-MoS$_2$ has quite large $e_{11}$, compared to that of other two monolayers. Interestingly, 1H-LaBr$_2$(FM) shows a negative $e_{11}$ which is also quite low compared to other materials. To understand the origin of piezoelectric constant, $e_{11}$ and $e_{12}$ can be decomposed into two parts[2, 23]:

$$e_{11} = e^{elc}_{11} + \sum_k e^{ion}_{11}(k) = e^{elc}_{11} + \sum_k \frac{e_0}{A} Z_{11}(k) \frac{d\eta_1}{d\eta_1}(1)$$

$$e_{12} = e^{elc}_{12} + \sum_k e^{ion}_{12}(k) = e^{elc}_{12} + \sum_k \frac{e_0}{A} Z_{11}(k) \frac{d\eta_2}{d\eta_2}(2)$$

The clamped-ion term ($e^{ion}_{11}$ or $e^{ion}_{12}$) arises from the contributions of electrons when the ions are frozen at their zero-strain equilibrium internal atomic coordinates ($u$); and the internal-strain ($e^{ion}_{11}$) terms arises from the contribution from internal microscopic atomic displacements in response to a macroscopic strain. In our case, the strain ($\eta$) is applied in the z-direction (see Figure 1). Here, $k$ runs over all the atoms in the unit cell, $a$ is the in-plane lattice constant, $e$ is the electron charge, and $A$ is the area as 2D unit is used. The Born effective charge ($Z_{11}$) of the $k$-th atom is calculated by the Berry-phase approach using DFPT. The response of the $k$-th atom’s internal coordinate along the z-direction ($u_1(k)$) in response to a macroscopic strain ($\eta_1$) is measured by $\frac{d\eta_1}{d\eta_1}$.

Table 2 shows that both $e^{elc}_{11}$ and $e^{ion}_{11}$ have same sign – positive – for 1H-MoS$_2$, unlike other two monolayers. This results in a large total $e_{11}$ for 1H-MoS$_2$. Note that other 1H-MX$_2$ (M = Mo, W and X = S, Se, Te) monolayers also exhibit positive $e^{elc}_{11}$ and $e^{ion}_{11}$.[17] However, due to the opposite sign of $e^{elc}_{11}$ and $e^{ion}_{11}$ in 1H-VS$_2$(FM), its total $e_{11}$ is smaller than the $e_{11}$ for 1H-MoS$_2$, even though it has a larger value of $e^{elc}_{11}$ (see Table 2).

Interestingly, 1H-LaBr$_2$(FM) shows a negative $e_{11}$, which is significantly larger than its $e^{elc}_{11}$, resulting in a negative total $e_{11}$. This is different from recently discovered negative piezoelectric co-efficient in layered ferroelectrics and wurtzite, where negative sign comes from $e^{elc}_{11}$. Here it is important to highlight that other 2D piezoelectrics – e.g., well-known h-BN monolayer[17] and 1H-VS$_2$ monolayer[24] – have negative $e^{ion}_{11}$, but $e^{elc}_{11}$ part dominates, resulting positive $e_{11}$.

Now to understand the origin of negative/positive $e^{ion}_{11}$, we expressed $e^{ion}_{11}$ in terms of $Z_{11}$ and $\frac{d\eta_1}{d\eta_1}$ (see eq.1). From Table 2, it is clear that the positive $e^{ion}_{11}$ in 1H-MoS$_2$ is due to unusual BEC of Mo and S as we see a negative (positive) sign for cation Mo (anion S) in BEC. Such counter-intuitive BECs – Mo (S) shows a negative (positive) dynamical charge, opposite to its static positive charge – are also reported for bulk 2H-MoS$_2$.[24].

Providing microscopic insight into the piezoelectric coefficients, BEC is – a dynamical charge – directly related to the change of electric polarization or dipole moment (for molecules) in response to an atomic displacement[23]. $Z_{11}$ is proportional to $\frac{\partial P_1}{\partial \eta_1(k)}$, where $\partial P_1$ is the change of dipole moment in z-direction induced by a small displacement of atom $k$ in the same direction ($\partial \eta_1(k)$)[23].

The negative slope ($\frac{\partial P_1}{\partial \eta_1(k)}$) will result 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 the the LO-TO splitting, which is the frequency difference between the longitudinal (LO) and transverse (TO) optical phonon modes[23].

Compared to 1H-LaBr$_2$(FM), the magnitude of $e^{ion}_{11}$ in 1H-MoS$_2$ and 1H-VS$_2$(FM) is smaller because of smaller BECs and $\frac{d\eta_1}{d\eta_1}$. We find that large negative $e^{ion}_{11}$ in 1H-LaBr$_2$(FM) originates from its large $Z_{11}$ and $\frac{d\eta_1}{d\eta_1}$, both terms are almost two times larger than those of 1H-MoS$_2$ or 1H-VS$_2$(FM). The large $\frac{d\eta_1}{d\eta_1}$ of 1H-LaBr$_2$(FM)
Table II. The electronic ($\epsilon_{\text{el}}^{12}$) and ionic ($\epsilon_{\text{ion}}^{12}$) part of the total piezoelectric stress constant $\epsilon_{11}$ in 2D piezoelectric unit $\text{pC/m}$, born effective charge $Z_{11}$ of M—Mo, V, and La and X—S and Br in $\text{pC/m}$, unit, where $e$ is the charge of an electron. Both 1H-VS$_2$ and 1H-LaBr$_2$ monolayers are in ferromagnetic (FM) state. $\frac{\Delta}{\Delta}$ represents the change of the position of the atoms along $a$-direction under a strain along $a$-direction ($\eta_i$).

|          | $\epsilon_{\text{el}}^{12}$ (pC/m) | $\epsilon_{\text{ion}}^{12}$ (pC/m) | $\epsilon_{11}$ (pC/m) | $Z_{11}$ (M) | $Z_{11}$ (X) | $\frac{\Delta}{\Delta}$ (M) | $\frac{\Delta}{\Delta}$ (X) |
|----------|----------------------------------|----------------------------------|---------------------|--------------|--------------|-----------------|------------------|
| 1H-MoS$_2$ | 315.000                          | 56.050                           | 371.050             | -1.006       | 0.503        | -0.037          | 0.018            |
| 1H-VS$_2$(FM) | 379.025                          | -80.925                          | 298.100             | 1.359        | -0.680       | -0.038          | 0.021            |
| 1H-LaBr$_2$(FM) | 111.175                          | -205.350                         | -94.175             | 2.540        | -1.269       | -0.069          | 0.035            |

Table III. Elastic constants ($C_{11}$ and $C_{12}$) in N/m, the ICOHP of a bond between cation (Mo/V/La) and anion (S/Br) in eV/bond unit, the Poisson’s ratio $\nu = C_{12}/C_{11}$ and piezoelectric strain coefficient in $d_{11} \text{pm/V}$.

|          | $C_{11}$ | $C_{12}$ | ICOHP  | $\nu$ | $d_{11}$ |
|----------|----------|----------|--------|-------|---------|
| 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    | -1.191 | 0.314 | -4.527  |

Now we calculate the piezoelectric stress constants ($d_{11}$) using $e_{ij}$ and elastic constants ($C_{ij}$) (see Table 3). First, the mechanical/elastic stability of ferromagnetic (FM) 1H-LaBr$_2$ monolayer is checked according to the criteria for a 2D hexagonal crystal structure:\[22\] $C_{11} > C_{12}$ and $C_{66} > 0$. Considering the two independent elastic constants (only two independent elastic constants due to space group P6m2 and two-dimensionality) that we obtain, namely $C_{11} = 30.34 \text{ N/m}, C_{12} = 9.53 \text{ N/m}$, (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\[14\]. Our calculated elastic coefficients for the monolayers are in good agreement with the previously reported values\[3, 8, 17\]. Compared to 1H-MoS$_2$ and 1H-VS$_2$(FM) monolayers, its lower $C_{11}$ and $C_{12}$ but larger $\nu$ indicate that 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 ICOHP approach\[27\], which mainly quantifies the strength of the covalency of a bond. The more negative ICOHP, the stronger the bonding. We see in Table 3 that 1H-LaBr$_2$(FM) monolayer has significantly weaker La-Br bond (bond length: 3.143Å), compared to that of Mo-S (2.417Å) or V-S (2.366Å) bond. Table 3 shows that $d_{11}$(again only independent coefficient due to symmetry and dimensionality; and $d_{11} = \epsilon_{11}^{\text{el}} - \epsilon_{12}^{\text{el}}$) of 1H-LaBr$_2$(FM) is about 22% larger than that of well-known 2D piezoelectric 1H-MoS$_2$ because former has quite low elastic constants. The origin of negative sign in $d_{11}$ of 1H-LaBr$_2$(FM) is in its negative $\epsilon_{11}$, which is discussed above.

Now we discuss how the magnetic ordering can affect on the piezoelectric response. We consider simple strip-type antiferromagnetic (AFM) order (see Figure 1). The calculated $\epsilon_{11}$ and $\epsilon_{12}$ are shown in Table 4. Interestingly, we find that $\epsilon_{11}$ is not equal to minus $\epsilon_{12}$ 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 1H-LaBr$_2$(AFM) is almost double compared to that of FM, however $\epsilon_{11}$ is still negative. To understand the origin of $\epsilon_{11} \neq -\epsilon_{12}$ for AFM, we consider two cases: (i) the structures (lattice parameters $a$ and $b$ and atomic positions) are relaxed, and (ii) AFM order is used, keeping lattice parameters $a$ and $b$ and atomic positions fixed in their FM structures, which are represented by * in Table 4. We see that it is the change in magnetic order that intrinsically causes $\epsilon_{11} \neq -\epsilon_{12}$ for AFM — not the structural changes associated to this magnetic order change, although the structural relaxation changes the values too. Both $\epsilon_{11}^{\text{el}}$ and $\epsilon_{11}^{\text{ion}}$ change in response to change in magnetic order. Table 4 also shows how the BECs and $\frac{\Delta}{\Delta}$ change, resulting in changes to $\epsilon_{11}^{\text{ion}}$.

IV. CONCLUSION

We show that 1H-LaBr$_2$ monolayer exhibits unusual in-plane negative piezoelectric coefficient, unlike many other 1H structured 2D piezoelectrics\[12, 15\]. Here the origin of negative piezoelectric coefficient is because of large negative $\epsilon_{11}^{\text{ion}}$ that can not be compensated by $\epsilon_{11}^{\text{el}}$; this is different from hitherto observed negative piezoelectric coefficients in some bulk materials due to large $\epsilon_{ij}^{\text{el}}$\[3, 8\]. 1H-LaBr$_2$ monolayer is a promising 2D piezoelectric,
having large piezoelectric $d_{11} (-4.527 \text{ pm/V})$ coefficient, which is comparable to that of well-known 2D piezoelectric 1H-MoS$_2$or 1H-VS$_2$ monolayers, and is larger than that of bulk wurtzite GaN ($d_{33} \approx 3.1 \text{ pm/V}$). We also explain the origin – both sign and magnitude – of the piezoelectric coefficients of three monolayers (1H-LaBr$_2$, 1H-MoS$_2$ and 1H-VS$_2$ monolayers) in terms of their dynamical charges (BECs) and atomic sensitivity ($\frac{d\sigma}{d\eta}$) to an applied strain. Being directly linked with $e_{ij}$, we believe that BECs – rather than static charge like Bader charge – can be good parameters for searching new 2D piezoelectrics, also providing insight into the underlying mechanism. Additionally, we show that change in magnetic order can affect on their piezo-response quite significantly, which can be a unique way for manipulating magnetism and electromechanical properties in 2D magnets.

|          | $e^{\text{elc}}_{11}$ | $e^{\text{ion}}_{11}$ | $e_{11}$ | $Z_{11}(M)$ | $Z_{11}(X)$ | $d_{11}(M)$ | $d_{11}(X)$ | $e^{\text{elc}}_{12}$ | $e^{\text{ion}}_{12}$ | $e_{12}$ | $d_{12}(M)$ | $d_{12}(X)$ |
|----------|----------------------|----------------------|----------|-------------|-------------|-------------|-------------|----------------------|----------------------|----------|-------------|-------------|
| 1H-VS$_2$* | 221.900              | -38.375              | 183.525  | 0.662       | -0.210      | -0.031      | 0.015       | 284.150              | 12.175               | -271.975 | 0.025       | -0.013      |
| 1H-VS$_2$ | 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$_2$ | 57.275              | -281.000             | -223.725 | 2.744       | -1.370      | -0.083      | 0.041       | -100.075             | 197.700              | 97.625   | 0.068       | -0.034      |

Table IV. The electronic ($e^{\text{elc}}_{11}$ and $e^{\text{elc}}_{12}$) and ionic ($e^{\text{ion}}_{11}$ and $e^{\text{ion}}_{12}$) part of the total piezoelectric stress constant $e_{ij}$ of antiferromagnetic 1H-VS$_2$ and 1H-LaBr$_2$ monolayer in 2D piezoelectric unit pC/m, born effective charge $Z_{11}(M)$ for Mo, V, and La and $X = S$ and Br in $|\sigma|$ unit, where $e$ is the charge of an electron. $\frac{d\eta}{d\sigma}$ represents the change of the position of the atoms along a-direction under a strain along b-direction ($\eta_2$). 1H-VS$_2$ (1H-LaBr$_2$) represents antiferromagnetic 1H-VS$_2$ (1H-LaBr$_2$) monolayer in its ferromagnetic structure (i.e., just the magnetic order is changed, no structural relaxation).

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