Abstract—Transition metal dichalcogenides (TMDs) in the form of nanolayers are very attractive for fundamental and promising for applied research. Applying a strain and a strain gradient to them makes it possible to tune their electric properties. The tuning can be explained by the presence of piezoelectric and flexoelectric effects. We considered the curved 2H-WS2 monolayer and analyzed its flexoelectric and piezoelectric properties using phenomenological Landau approach and the density functional theory. The strain, strain gradient, and dipole moment values in atomic arrangement coordinates were calculated. The dependences of these parameters on the longitudinal axis of the layer were fitted. From these dependences the components of the flexoelectric and piezoelectric tensors have been determined and analyzed. The obtained results are useful for the applications of LD-TMDs in strain engineering and flexible electronics.

Keywords—flexoelectric effect, TMD monolayer, strain gradient

I. INTRODUCTION

Transition metal dichalcogenides (TMDs) attract interest of researchers due to their thickness-dependent electrical and optical properties. In the bulk form TMDs are usually non-polar semiconductors with a fairly wide band gap (≈1.1 – 2 eV) and a specific shape of the Fermi surface [1]. The electro-physical properties of TMD nanoparticles can vary, from the direct-band semiconductor to metallic conductivity [2], and from the non-polar state to the ferroelectric one [3]. Although the TMD nanolayers possess a 2D planar structure like graphene, their physical, chemical, and electronic properties are different from those of graphene.

There are possibilities for tuning the polar, structural and electronic properties of low dimensional transition metal dichalcogenides (LD-TMDs) by application of either inhomogeneous curvature-induced strain gradients [4] or homogeneous elastic strains [5]. In particular, Duerloo et al. [2] predicted a strain-induced phase transition from a semiconducting 2H phase to a metallic 1T’ one in various MX2 monolayers. The effect of strain and strain gradient on LD-TMD polar and electronic properties can be essential for the control of the properties. The physical origin of the bending-induced changes of LD-TMDs electronic and polar properties can be similar to the ones in bended graphene and boron nitride, and in this case the flexoelectric effect plays a very important role [6]. The property changes are highly dependent on the curvature. Thus it is possible to achieve a sufficiently large polarization caused by a flexoelectric effect in LD-TMD if they are strongly curved [7].

Kang et al. [4] observed enhanced conductivity and tunable out-of-plane piezoelectricity in 2H-MoTe2 flakes caused by surface corrugation. The experimental results were corroborated by their ab initio calculations, analytical calculations performed within Landau-Ginzburg-Devonshire (LGD) approach [8] and finite element modeling (FEM) [9]. LGD approach explores polarization with the flexoelectric origin induced by bending and by inversion symmetry breaking due to the interactions with the substrate. The FEM made it possible to calculate the electric and elastic fields, polarization caused by flexoelectric coupling, and its correlation with free charge density for a TMD nanoflake placed on a substrate with a sinusoidal corrugation profile [10].

Despite the intense research of LD-TMDs, there is no complete information about their flexoelectric and piezoelectric tensors. Moreover, the influence of the and numerical values of symmetry tensor components on polar and electronic phenomena in LD-TMDs have not been studied. The knowledge about the couplings in LD-TMDs is important to predict and control their physical properties for innovative applications in advanced memories and nanoelectronics. In this paper, using the phenomenological Landau approach and the density functional theory (DFT), we consider the corrugated monolayer of 2H-WS2. The nonzero components of its flexoelectric and piezoelectric coupling tensors are calculated. The possible dependence of their
coupling tensors on the surface-induced symmetry lowering and corrugation layer have been analyzed.

II. AB INITIO CALCULATIONS

We performed the calculations of the position of atoms in the WS\(_2\) monolayer (Fig. 1 a,b) for two cases: a flat layer and a 10% corrugated layer. Ab initio calculations were made in the same way as in [10] within the DFT in the generalized gradient approximation, implemented in the Quantum Espresso code. However, in this case the following parameters were used:

- PAW pseudopotentials included 14 valence electrons for wolfram (W) and 6 valence electrons for sulfur (S);
- the integration of the Brillouin zone has been performed using 15x15x1 \(k\)-points mesh;
- the initial (flat) layer was built with the experimental value of the lattice constant of 3.161 Å and contained 48 atoms.

For the corrugated layer, the lattice constant of the supercell in \(x\)-direction was reduced and the atomic \(z\) (out-of-plane) coordinates were modulated by suitable sinusoidal distribution to match the integer value of corrugation. After that, all the systems were relaxed through all the internal coordinates until the Hellmann-Feynman forces became less than \(10^{-4}\) atomic units, and at this point all the necessary quantities (atomic coordinates and wave functions) were extracted. The corrugation obtained for the relaxed system differs from the initial corrugation by no more than a few percent. Therefore, the calculations revealed that the bending in \(z\)-direction is sinusoidal along the \(x\)-axis.

In addition, the Bader charges were computed. The charges distribution in a flat system appeared to be uniform and equal to \(Q_w = 1.376e\) for wolfram atoms, and to \(Q_s = -0.688e\) for sulfur atoms, where \(e = 1.602 \cdot 10^{-19}C\) is the elementary charge. For stronger curved layers with a 10% bending, a harmonic dependence of the charges on the \(x\)-coordinate was observed. (see Fig. 2).

The results shown in Fig. 2 are similar to the bending-induced redistribution of Bader charges in phosphorene and graphene nanoribbons [6]. It appeared that the action of the applied strain gradient breaks the symmetry of the Bader charges. However, our calculations of Bader charges redistribution for WS\(_2\) (Fig. 2) and MoS\(_2\) [10] reveal that the charges are much smaller than the ones in phosphorene and graphene [6]. The possible reason is the small discrepancy in the net Bader charges of sulfur in a bended WS\(_2\) monolayer. For this reason, the effect of the charge distribution on the electrophysical parameters of the WS\(_2\) layer can be neglected.

III. FLEXOELECTRIC COEFFICIENTS

The static electric polarization of a WS\(_2\), \(P_i(\vec{x})\), has the form:

\[
P_i(\vec{x}) \equiv f_{ijkl} \frac{\partial u_{ij}}{\partial x_k} + e'_{ijk} u_{jk} - \varepsilon_0 \omega_{ij} \frac{\partial \varphi}{\partial x_k}
\]  

Here \(f'_{ijkl}\) is the flexoelectric tensor, \(u_{ij}(\vec{x})\) is the elastic strain tensor, \(e'_{ijk}\) is the piezoelectric tensor, and \(t\) is the
nanoflake thickness, $\partial \phi / \partial x_j$ is the gradient of electric potential, $\varepsilon_0$ is a universal dielectric constant, $\chi_{ij}$ is a real part of the TMD dielectric susceptibility. Einstein summation over repeated indexes is used hereinafter.

$$d_x(x) = e_{xxx}u_{xx}(x) + e_{xx}u_{x,x}(x) + f_{xxx}u_{x,x,x}(x),$$  \hspace{1cm} (2) $$d_y(x) = e_{xxx}u_{xx}(x) + e_{xx}u_{x,x}(x) + f_{xxx}u_{x,x,x}(x),$$  \hspace{1cm} (3)

here $d_i(k)$ are $i$-axis projections of the elementary dipole moment; $e_{ijk}$ and $f_{ijkl}$ are the components of the piezoelectric and flexoelectric tensors in Cartesian coordinates; $u_{ij}$ and $u_{ijk}$ are the strain and strain gradient tensors, respectively. Since the out-of-plane dipole moment is more informative, we will consider only the $z$-axis projection $d_z(x)$.

To determine piezoelectric and flexoelectric tensors from expressions (2) and (3), the strain and strain gradient tensors of each set of atoms, which we call a dipole (see Fig. 1c), are necessary to know. The dipole moment $\vec{d}$ was calculated from the following equation:

$$\vec{d}^{(i)} = \frac{z^{(i)}}{W}Q_{W} + \frac{1}{3} \sum_{k=1}^{6} \vec{r}_{Sk}^{(i)}Q_{S},$$  \hspace{1cm} (4)

where $\vec{r}_{Sk}^{(i)} = \{x_{S_{k}}, y_{S_{k}}, z_{S_{k}}\}^{(i)}$ and $\{x_{W}, y_{W}, z_{W}\}^{(i)}$ are position vector of the W and S atoms, respectively for $i$-th dipole in the monolayer. Coefficient $1/3$ is due to the fact that each sulfur (S) atom is bonded simultaneously with 3 wolfram (W) atoms, thereby each W is 1/3 charge of S.

To determine strain tensor $u_{ij}$ and strain gradient $u_{ijk}$ was necessary to know elementary displacement $\vec{U}$ of the mass centers. For a 10% corrugated layer $\vec{U}$ was calculated from:

$$\vec{U}^{(ij)} = \vec{U}^{(ij)}_{W} - \vec{U}^{(ij)}_{S},$$  \hspace{1cm} (5)

where $\vec{U}^{(ij)}_{W}$ is the position vector of $i$-th dipole in the flat layer, $\vec{U}^{(ij)}_{S}$ is the position vector of $i$-th dipole in the layer with 10% of corrugation. The position vector of a given dipole is determined by the equation:

$$\vec{r}^{(ij)} = \frac{1}{m_{W} + 6 m_{S}} \left( \vec{r}^{(ij)}_{W}m_{W} + \sum_{k=1}^{6} \vec{r}^{(ij)}_{Sk}m_{S} \right),$$  \hspace{1cm} (6)

where $i$ is the dipole number, $j$ is the percentage of corrugation, $m_{W} = 183.8 \text{ g/mol}$ is atomic masses of wolfram and $m_{S} = 32 \text{ g/mol}$ is atomic masses of sulfur.

The dependences on the $x$ coordinate of the $z$-projection of the dipole moment (4) and the $z$-projection of the elementary displacement (5) were determined from $ab\ initio$ calculations indicated by points in Fig. 3(b) and 3(a), respectively. The dependences $U_{z}(x)$ and $d_{z}$ were fitted by analytical expressions:

![Fig. 3. The dependences on the $x$ coordinate of (a) the elementary displacement $U_{z}$; (b) the elementary dipole moment $d_{z}$; (c) the strain tensor component $u_{xx}$ calculated according to Eq.(7) and (d) the strain gradient component $u_{xx,x}$ calculated according to Eq.(8). The points in the plots (a) and (b) are the discrete values calculated from Eqs.(4)-(6), the solid curves are the fit of these values according to Eqs.(7) and (8). The fitting parameters are given in Table I.](image-url)
where the coefficients $U_0$, $d_{zc}$, $d_{zs}$ and $k$ are fitting parameters, which numerical values are selected to reach the best fit of the points and are given in Table I.

The dependences obtained according (7) – (8) shown by solid curves in Fig. 3 (a) and (b).

from which we get:

$$f_{3131} = -\frac{2d_{zc}}{U_0 k^2}, \quad e_{331} = -\frac{2d_{zs}}{U_0 k}$$

The values of $f_{3131}$, and $e_{331}$ are listed in the Table I.

CONCLUSION

Using DFT ab initio calculations combined with phenomenological Landau approach, we consider the charge state and the atomic displacements of the corrugated 2H-WS2 monolayer, and determine the effective components of its flexoelectric and piezoelectric coupling tensors.

The results of our calculations showed that the contribution of the flexoelectric effect prevails over the piezoelectric effect in the out-of-plane directions of the monolayer. This means that a practical strain gradient (about 1 nm$^{-2}$) can induce higher flexoelectric response compared to the piezoelectric response.

Surprisingly, our calculations of Bader charges redistribution in a bended WS2 reveal that the charges are much smaller than the ones in phosphorene and graphene. The possible reason is the small discrepancy in the net Bader charges of sulfur in the bended WS2 monolayer.

The obtained results can be useful for application bended WS2 layers in the elaboration of nanosized flexible electronic devices.

The corrugation profile of the WS2 layers can control the sharpness of p-n junctions between the regions with n-type (e.g., hump-like sections) and p-type (valley-type sections) conductivity. Therefore, their curved monolayers are promising candidates for ultra-small bipolar transistors and diodes.

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The dependence of $U_v(x)$ has half the period of harmonic function, so we can conclude that $e_{xxx} = 0$ and $f_{xxx} = 0$.

The displacement caused the strain tensor can be determined as $u_{jk} = \frac{1}{2} \left( \frac{\partial u_j}{\partial x} + \frac{\partial u_j}{\partial x} \right)$, thus, from (7) we obtain the following equation and its nonzero derivatives:

$$u_{xx}(x) = u_{xx}(x) = \frac{1}{2} \frac{\partial U_v}{\partial x} = -\frac{U_0}{2} k \sin(kx), \quad (9)$$

$$u_{xx}(x) = u_{xx}(x) = -\frac{U_0}{2} k^2 \cos(kx), \quad (10)$$

The dependences calculated from Eq. (9) – (10) are shown in Fig. 3 (c) and (d).

Substituting the functions from (7) – (10) to (2), we obtain equation for nonzero components of flexoelectric and piezoelectric coefficients:

$$d_{zc}\cos(kx) + d_{zs}\sin(kx) = -e_{331} \frac{1}{2} U_0 k \sin(kx) - f_{3131} \frac{1}{2} U_0 k^2 \cos(kx), \quad (11)$$

AUTHORS’ CONTRIBUTION

H.V.S. performed the mathematical processing and fitting of the DFT results and wrote the manuscript draft. A.N.M. and S.O.Y. generated the research idea; A.N.M. evolved the analytical model, interpreted the results; S.O.Y. stated the problem for DFT calculations, evolved the procedure of their physical processing and interpret the results. I.K. performed DFT calculations. K.L.M. prepared figures. G.I.D., K.L.M. and G.S.S. worked on the manuscript improvement.

REFERENCES

[1] Z. Xu et al., “Topical review: Recent progress of charge density waves in 2D transition metal dichalcogenide-based heterojunctions and their applications,” Nanotechnology, vol. 32, no. 49. Sep. 2021.

[2] K.-A. N. Duerloo, Y. Li, and E. J. Reed, “Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers,” Nat. Commun., vol. 5, no. 1, p. 4214, Sep. 2014.

[3] J.-H. Choi and S.-H. Jhi, “Origin of robust out-of-plane ferroelectricity in d1T-MoS2 monolayer,” J. Phys. Condens. Matter, vol. 32, no. 4, p. 045702, Jan. 2020.

[4] S. Kang et al., “Tunable Out-of-Plane Piezoelectricity in Thin-Layered MoTe2 by Surface Corrugation-Mediated Flexoelectricity,” ACS Appl. Mater. Interfaces, vol. 10, no. 32, pp. 27424–27431, Aug. 2018.

[5] J. Berry, S. Zhou, J. Han, D. J. Srolovitz, and M. P. Haataja, “Domain morphology and mechanics of the H/T’ transition metal dichalcogenide monolayers,” Phys. Rev. Mater., vol. 2, no. 11, p. 114002, Nov. 2018.

[6] P. Pandey, L. Covaci, and F. M. Peeters, “Tuning flexoelectricity and electronic properties of zig-zag graphene nanoribbons by functionalization,” Carbon N., vol. 171, pp. 551–559, Jan. 2021.

[7] W. Shi, Y. Guo, Z. Zhang, and W. Guo, “Flexoelectricity in Monolayer Transition Metal Dichalcogenides,” J. Phys. Chem. Lett., vol. 9, no. 23, pp. 6841–6846, Dec. 2018.

[8] A. N. Morozovska, E. A. Eliseev, G. I. Dovbeshko, M. D. Glincuk, Y. Kim, and S. V. Kalinin, “Flexoinduced ferroelectricity in low-dimensional transition metal dichalcogenides,” Phys. Rev. B, vol. 102, no. 7, p. 075417, Aug. 2020.

[9] A. N. Morozovska et al., “Correlation Between Corrugation-Induced Flexoelectric Polarization and Conductivity of Low-Dimensional Transition Metal Dichalcogenides,” Phys. Rev. Appl., vol. 15, no. 4, p. 044051, Apr. 2021.

[10] H. V. Shevlakova, S. O. Yesylevskyy, I. Kapchuk, G. I. Dovbeshko, Y. Kim, and A. N. Morozovska, “Flexoelectric and Piezoelectric Coupling in a Bended MoS2 Monolayer,” Symmetry (Basel), vol. 13, no. 11, p. 2086, Nov. 2021.