Gate-tunable chiral phonons in low-buckled group-IVA monolayers

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Abstract

We investigate the electric response of chiral phonons on the low-buckled group-IVA monolayers by performing first-principles calculations. The vertical electric field breaks the degeneracy of phonon modes at high-symmetry $\pm K$ points of the phonon Brillouin zone, and the size of the phononic gap is proportional to the strength of the electric field. The gapped phonon modes at $\pm K$ possess chiralities with considerable phonon circular polarizations and discrete phonon pseudoangular momenta. The chiralities of phonons are robust against the variation of the field strength, but reversed by changing the field direction. Electric control of chiral phonons adds a new dimension to the study of chiral phonons, which has potential use in the design of phononic and valley devices.

Keywords: chiral phonons, gate control, first-principles calculations

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)

1. Introduction

In condensed matter physics, spatial inversion symmetry breaking usually endow chirality to Bloch electrons and other quasiparticles. For electronic systems, chiralities of valley electrons have been observed in transition metal dichalcogenide (TMDC) monolayers through optoelectronic measurements [1–4]. Recently, chiral phonons with atomic circular vibrations have been proposed theoretically in honeycomb lattice with broken inversion symmetry [5] and verified experimentally in TMDC by optical pump–probe techniques [6]. The chiral phonons are different from the conventional phonons with linear atomic vibrations. The circular vibrations of chiral phonons can give rise to nonzero phonon circular polarizations and extra angular momenta besides well-known spin/orbital angular momentum [7, 8]. They participate in intervalley scattering of electrons [6, 9–11] or couplings with other quasiparticles [12–16], and enable phonon-driven topological states [17]. The novel characteristics of chiral phonons exhibit conceptual significance and application potential.

After chiral phonons become recognized, a consequent intriguing question is how to selectively acquire phonons with opposite chiralities. The selection of chiralities introduces a tunable degree of freedom to chiral-phonon-involved physical processes and also facilitates information encoding [6, 9, 12–16]. Chiralities of phonons usually originate from pristine materials without inversion symmetry in their crystalline point groups [6] or structural symmetry reduction by e.g. proximity effect [18], thus it is hard to tune chiralities in a controllable way. On the other hand, compared with bulk materials, the properties of monolayer materials can be easily modulated by applying vertical electric field [19, 20]. Specific to low-buckled group-IVA monolayers [21–25], there are two atomic layers that feel different static electric potentials under...
vertical electric fields, where the inversion symmetry is broken even though the structural change is absent. Accordingly, the degeneracies, band topology and spin polarizations in their electronic structures can be modulated by vertical electric field [26, 27]. By analogy to electronic systems, it is promising to use electric fields to control phonons and their chiralities, which is worth studying carefully.

In this paper, we use first-principles calculations to investigate the electric field effects on chiral phonons of low-buckled group-IVA monolayers, where silicene, germanene and stanene are considered. For degenerate branches, phononic gaps are opened and increased with external electric fields. Gapped phonon modes with atomic circular motions are computed to have considerable phonon circular polarizations and discrete phonon pseudoangular momenta. Moreover, when turning around the direction of electric fields, the chiralities of phonons are also reversed. Our work provides a new route to control chiral phonons conveniently.

The rest of this paper is organized as follows. In section 2, we provide the details on density functional theory calculations of low-buckled group-IVA monolayers. Definitions and the characterization methods of chiral phonons are introduced as well. In section 3, we investigate the influence of electric fields on crystal structures, phonon dispersions and vibration modes, demonstrating the tunability of phonon chiralities. Conclusions are made in section 4.

2. Computational details

2.1. Density functional theory calculations

Density functional theory calculations of the low-buckled group-IVA monolayers are performed using projector augmented wave method [28] as implemented in Vienna Ab initio Simulation Package [29]. The generalized gradient approximation of Perdew–Burke–Ernzerhof functional [30] is adopted to describe the exchange and correlation effects of electrons. The energy cutoff is set to 500 eV. To avoid interactions between the monolayer and its periodic images, a vacuum space larger than 24 Å is inserted. A Monkhorst–Pack k-mesh of 17 × 17 × 1 is used in structural relaxations. As for the calculations of phonon properties, we employ the finite displacement method [31] using PHONOPY package [32], where a 5 × 5 × 1 supercell and a 5 × 5 × 1 k-mesh are adopted. To simulate an applied vertical electric field, a sawtooth-like wave field is used [33].

2.2. Characterizations of chiral phonons

To illustrate the chirality of phonons conveniently, the basis set to describe phonon eigenvectors is transformed from the Cartesian coordinate to a new orthogonal coordinate. For low-buckled group-IVA materials, there are two atomic sites labeled by A and B in a unit cell, as shown in figure 1(a).

As a result, the new basis set contains six unit vectors, i.e. $|R_A⟩ \equiv \frac{1}{\sqrt{2}}(1, i, 0, 0, 0, 0)^T$, $|L_A⟩ \equiv \frac{1}{\sqrt{2}}(1, -i, 0, 0, 0, 0)^T$, $|Z_A⟩ \equiv (0, 0, 1, 0, 0, 0)^T$, $|R_B⟩ \equiv \frac{1}{\sqrt{2}}(0, 0, 0, 1, 0, 0)^T$, $|L_B⟩ \equiv \frac{1}{\sqrt{2}}(0, 0, 0, 0, 1, 0)^T$, $|Z_B⟩ \equiv (0, 0, 0, 0, 0, 1)^T$, where $|R_{A(B)}⟩$, and $|Z_{A(B)}⟩$ represent the unit vectors of right-handed circular motion, left-handed circular motion and the z-direction linear motion for atomic vibrations on a A(B) sublattice, respectively. A phonon eigenvector $|ξ⟩$ can be represented in this new basis set as,

$$|ξ⟩ = \sum_{α=A,B} (C_{R_α}|R_α⟩ + C_{L_α}|L_α⟩ + C_{Z_α}|Z_α⟩),$$

where $C_{R_α} = ⟨R_α|ξ⟩$, $C_{L_α} = ⟨L_α|ξ⟩$, $C_{Z_α} = ⟨Z_α|ξ⟩$. Considering the normalization condition of $|ξ⟩$, $\sum_{α=A,B} (|C_{R_α}|^2 + |C_{L_α}|^2 + |C_{Z_α}|^2)$ should be equal to 1.

Then we define the operator of phonon circular polarization along the +z direction as,

$$S_\phi^z \equiv \sum_{α=A,B} (|R_α⟩⟨R_α| - |L_α⟩⟨L_α|).$$

The chirality of a phonon eigenvector $|ξ⟩$ can be characterized by the phonon circular polarization,

$$S_\phi^z = |ξ⟩⟨S_\phi^z|ξ⟩ = \sum_{α=A,B} (|C_{R_α}|^2 - |C_{L_α}|^2).$$

The module of $S_\phi^z$ represents the magnitude of chirality, and its sign represents the direction of chirality. According to the definition, $S_\phi^z$ is exactly +h(−h) for a phonon mode with fully right-handed (left-handed) chirality.

3. Results and discussions

3.1. Crystal structure

Among the two-dimensional group-IVA materials, the crystal structures of silicon, germanene, and stanene considered here have honeycomb lattice, as illustrated in top view of figure 1(a). In side view of figure 1(b), two atomic sites in a unit cell are located in two atomic layers of different heights along the

|       | Silicene | Germanene | Stanene |
|-------|----------|-----------|---------|
| $a$ (Å) | 3.87     | 4.06      | 4.67    |
| $Δ$ (Å) | 0.45     | 0.69      | 0.85    |

Figure 1. Crystal structure of a low-buckled group-IVA monolayer. The top view and the side view are given in (a) and (b), respectively. The dashed box represents one unit cell, and blue balls denote group-IVA atoms. The computed lattice constants $a$ and height differences $Δ$ of three group-IVA monolayers after structural relaxation are also listed.
z axis, exhibiting a buckled structure. The buckled honeycomb structure has a crystalline point group of $D_{6h}$, in contrast to flat graphene monolayer with $D_{6h}$ group [34]. We computed lattice constant, $a$, and height difference, $\Delta$, of buckled atomic layers for three monolayers in the absence of electric field, which are listed in figure 1 and agree with previous calculation results [21–25]. From silicene to stanene, the bigger is the atomic number, the larger is the lattice constant and the height difference. It is also seen that buckling degree gradually becomes larger with increasing ratio of $\Delta$ to $a$, i.e. 0.12, 0.17, and 0.18 for three monolayers. For graphene with $sp^2$ bonds, the ratio is zero, while $sp^3$ hybridization leads to a ratio of 0.20. Therefore, the bonds of these three monolayers are regarded as a mix of $sp^2$ and $sp^3$ hybridizations [22, 23].

We also computed the fully relaxed geometric structures of three monolayers, under vertical electric fields up to 0.2 V Å$^{-1}$. Compared with pristine monolayers, the deviations of the lattice constant and the height differences are less than 1% and 3%, respectively. Therefore, it is found that the influence of electric fields on geometric structures is tiny.

### 3.2. Phononic gap opening at K point under electric fields

Taking silicene as a prototype of low-buckled group-IVA monolayer, figure 2(a) shows its phonon dispersion without applied electric field, which is presented by black solid lines. The phonon dispersions of germanene and stanene can be found in figure S1 of the supplementary material (https://stacks.iop.org/JPCM/33/285704/mmedia), and they are similar to that of silicene. There is no imaginary frequency in phonon dispersions, indicating that the crystal structure is stable dynamically. At $\Gamma$ point, there are three degenerate acoustic branches with zero frequency and three optical branches above them. For optical branches, they can be divided into two groups, i.e. one branch with lower frequency of 185 cm$^{-1}$ and two degenerate branches with higher frequency of 553 cm$^{-1}$. At the high-symmetry $K$ point, there are two doubly-degenerate modes, and two nondegenerate modes.

In the following part, we focus on the degenerate modes, which belongs to acoustic branches with frequency of 104 cm$^{-1}$ and optical branches with frequency of 404 cm$^{-1}$, respectively.

Under vertical electric fields, the phonon dispersion of silicene monolayer is shown by dashed red lines in figure 2(a). The imaginary frequency is also absent in phonon dispersions, and the crystal structure is still stable. The phonon dispersion has no obvious changes, except for previous degenerate points at $K$. Figures 2(b) and 2(c) zoom in on rectangular boxes of figure 1(a), showing the evolution of phonon dispersions around $K$ for acoustic branches and optical branches that we focus on. Both doubly degenerate branches at $K$ point are split in frequency with gap openings. Under a vertical electric field of $E_z = 0.1$ V Å$^{-1}$, the phononic gaps of acoustic and optical branches are 0.93 cm$^{-1}$ and 0.03 cm$^{-1}$, respectively. It is the spatial inversion symmetry breaking under the action of applied electric field that lifts the degeneracy in the spectra [26, 27].

Figures 3(a) and 3(b) demonstrate the evolution of phononic gaps with the electric field strength for acoustic and optical branches, respectively, where three monolayers are all considered. These gaps are linearly proportional to applied electric field, that is, the linear relationship is independent of monolayers and phonon branches. Moreover, for acoustic branches in figure 3(a), the ratio of the gap to the electric field strength decreases with increasing atomic numbers. In contrast, for optical branches in figure 3(b), the dependence between ratios and atomic numbers is reversed. Comparing gaps between acoustic branches and optical branches, the former is much larger than the latter one. Besides, different from $K$ point, the degeneracies at $\Gamma$ are unchanged.

### 3.3. Gate-tunable chiral phonons at K point

We then investigated atomic vibrations of different phonon modes and their chiralities under vertical electric fields. Figure 4(a) shows vibrations of six phonon modes at $\Gamma$ in a unit cell of silicene. For each phonon mode, both atoms in a unit cell are linearly vibrated. As for acoustic modes, interatomic relative motions are absent, while they are present for optical modes. Three acoustic (optical) modes are further distinguished by three directions of atomic vibrations, i.e. out-of-plane direction, longitudinal in-plane direction along the bond, and transverse in-plane direction. According to their atomic
Figure 3. Evolutions of phononic gaps with the field strength for three group-IVA monolayers. (a) Acoustic phononic gaps; (b) optical phononic gaps.

Figure 4. Atomic vibrations in a unit cell for phonon modes under an electric field. (a) Phonon modes at $\Gamma$. (b) Phonon modes at $K$. Both (a) and (b) include six panels, corresponding to atomic vibrations of different phonon modes. For each panel, two blue balls represent silicon atoms in a unit cell. The radius of the circular trajectory around an atom is proportional to the amplitude of atomic circular vibration. The curved arrow near the circular trajectory represents the direction of rotation. The point and cross on an atom represent opposite linear vibrations along the $z$ axis.

Moving on the $K$ point, corresponding atomic vibrations of six phonon modes are listed in figure 4(b). It is seen that the circular atomic vibrations appear besides linear ones. Since the above nomenclature of phonon modes at $\Gamma$ is not appropriate for the modes at $K$, we differ these phonon modes at $K$ by their frequencies in the ascending order for simplicity. The third and sixth modes only possess circular vibrations in $xy$ plane. For these two modes, two atoms in a unit cell are clockwise and anticlockwise vibrated, respectively, but with same amplitude. Their computed $S_{\text{ph}}^z$ are zero as well, even though circular vibrations are present. It is because the polarization cancellation of opposite circular motions of two atoms in a unit cell.

More interestingly, for the rest modes at $K$ corresponding to previous gapped branches, one atom in a unit cell exhibits linear vibration along the $z$ axis, while the other is circularly vibrated. For gapped acoustic branches, the circular motions are opposite in the first and second modes. The same applies to the fourth and fifth modes of gapped optical branches. Comparing with those of acoustic modes, the amplitudes are larger for circular vibrations of optical modes. Based on the above atomic vibrations, the $S_{\text{ph}}^z$ under different electric fields were computed, and their values can be found in figure 5. The computed $S_{\text{ph}}^z$ are no longer vanishing, with considerable values, thus corresponding phonon modes exhibit definite chiralities. Under a certain electric field, gapped modes have opposite circular polarizations for both acoustic and optical branches. Therefore, for gapped modes, only the branch with lower frequency is shown in figure 5, with (a) and (b) corresponding to acoustic and optical cases, respectively. Comparing with those of acoustic branches, gapped modes of optical branches have much larger the magnitude of $S_{\text{ph}}^z$ due to their stronger amplitudes of circular motions. Besides, the amplitudes of linear vibrations along the $z$ direction for gapped acoustic branches are much larger than those of the gapped optical branches, which are shown in figure S2 in the supplementary material. The stronger vertical vibrations lead to larger changes of electric potential energies under vertical electric vibrations.
3.4. Discussions

We investigate the gate-tunable chiral phonons at $K$ above. There is another high-symmetry $-K$ point, which is related to the $K$ point by time-reversal symmetry [1, 3]. The computed phonon dispersions and chiralities at $-K$ are given in the supplementary material. The phonon frequencies and gap evolutions are the same at $-K$ as those at $K$. In contrast, for phonon modes with the same frequency, the computed $S_{\text{ph}}^z$ and PAM at $-K$ are opposite to those at $K$, demonstrating contrasting phonon chiralities. Both the frequency degeneracy and opposite chiralities are ensured by time-reversal symmetry. Moreover, compared with graphene monolayers, low-buckled group-IVA monolayers have larger spin-orbital couplings. The spin-orbital coupling is not taken into account in the above DFT calculations. We show the results with the spin-orbital coupling considered in the supplementary material. Our conclusions on phonon dispersions and chiralities are robust against the spin-orbital coupling.

Given that PAM can contribute a selection rule [5, 6, 9], the chiral-phonon-assisted optical transition can also be modulated by applied electric field. When PAM becomes opposite under reversed electric field, the chirality of applied optical field is expected to be changed correspondingly to enable the optical transition. Moreover, domains with opposite phonon chiralities are likely to be formed by applying opposite gates on different regions of a group-IVA monolayer, which will give rise to topological protected one-dimensional thermal transport channels along the domain boundary [35, 36]. By patterning opposite gates, a grid of thermal transport channels can be further fabricated and used to design nanoscale phononic and valley devices. In addition, two-dimensional ferroelectric materials are also worth study [37], since they have stronger response in structure to electric field that may further boost the phononic gap.

4. Conclusions

In summary, we performed first-principles calculations to investigate the effect of vertical electric fields on chiral phonons in low-buckled group-IVA monolayers. Since the vertical electric field breaks spatial inversion symmetry, phononic...
gaps are opened at high-symmetry $\pm K$ points of the momentum space. The magnitudes of phononic gaps increase linearly with the electric field strength, and group-IVA monolayers considered here exhibit different increasing rates. At $\pm K$, definite chiralities, characterized by considerable circular polarizations and discrete PAM, are generated for the gapped phonon modes. The chiralities of phonons become opposite by turning around the direction of vertical electric fields. The gate-tunable chiral phonons are expected to be involved in modulations of e.g. optical transitions and thermal transports, offering opportunities for investigating couplings of chiral phonons with other quasiparticles and exploiting related devices.

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Data availability statement

All data that support the findings of this study are included within the article and the supplementary material.

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