Unusual electric polarization behavior in elemental quasi-2D allotropes of selenium

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We investigate tunable electric polarization and electronic structure of quasi-two-dimensional (quasi-2D) allotropes of selenium, which are formed from their constituent one-dimensional (1D) structures through an inter-chain interaction facilitated by the multi-valence nature of Se. Our \textit{ab initio} calculations reveal that different quasi-2D Se allotropes display different types of electric polarization, including ferroelectric (FE) polarization normal to the chain direction in \(\alpha\) and \(\delta\) allotropes, non-collinear ferrielectric (FiE) polarization along the chain axis in \(\tau\)-Se, and antiferroelectric (AFE) polarization in \(\eta\)-Se. The magnitude and direction of the polarization can be changed by a previously unexplored rotation of the constituent chains. In that case, an in-plane polarization direction may change to out-of-plane in \(\alpha\)-Se and \(\delta\)-Se, flip its direction, and even disappear in \(\tau\)-Se. Also, the band gap may be reduced and changed from indirect to direct by rotating the constituent chains about their axes in these quasi-2D Se allotropes.

I. INTRODUCTION

It is not widely known that the term \textit{ferroelectric} (FE) has been coined already in 1912 by Erwin Schrödinger as an electric counterpart to a ferromagnet [1]. At low enough temperatures, ferromagnetic or ferroelectric behavior is manifested by a permanent magnetic or electric polarization of a material that changes its direction upon applying an external field during a hysteretic process. Less than a decade after Schrödinger dismissed – immediately after proposing it – the concept of ferroelectricity as unrealistic, ferroelectric behavior was identified experimentally in Rochelle salt [2, 3]. There is a long way from Rochelle salt to new, low-dimensional ferroelectrics that have captured the attention of the scientific community by their complex behavior and their potential application in electronics. This is particularly true for recently discovered 2D `van der Waals' (vdW) layered structures with ferroelectric behavior and different origins of polarization [4–8]. Best-known displacive ferroelectrics derive their behavior from a relative displacement of sublattices, which is characterized by the position of a representative atom within the unit cell. Changes in polarization, typically along a given direction, may be caused by applying an external electric field, such as in thin-film BaTiO\(_3\) [9, 10]. Only in specific 3D materials including PbTiO\(_3\) [11], a strain gradient has been shown to modify the electrical polarization by an effect sometimes dubbed `flexoelectricity' [12]. Flip of the polarization direction has been observed in 2D vdW systems, such as ZrI\(_2\), where shear strain has changed the symmetry of the system [13, 14]. In these systems, whether due to an external electric field or mechanical strain, polarization changes have been limited to changes in the magnitude, whereas the polarization direction remained the same or flipped by 180°. Capability to modify both magnitude and direction of polarization will open a whole new perspective for the application of 2D FE materials.

In this study, we investigate the polarization and band structure of four quasi-2D allotropes of Se, which we call \(\alpha\)-Se, \(\delta\)-Se, \(\eta\)-Se and \(\tau\)-Se. These quasi-2D allotropes are formed from their constituent one-dimensional (1D) compounds we call the \(a\)-helix, \(b\)-chain, \(c\)-helix and \(\tau\)-chain, which possess a rotational degree of freedom about their axis. All atoms in the isolated 1D structures have two neighbors at the same distance and are structurally as well as electronically equivalent. In the quasi-2D allotropes, however, differences arise among individual atoms due to the inter-chain interaction. Our \textit{ab initio} density functional theory (DFT) calculations reveal that the Bader charge of inequivalent Se sites deviates from six valence electrons, indicating the possibility of a macrosopic electric polarization.

As we will discuss further on, we find a FE polarization in \(\alpha\)-Se and \(\delta\)-Se, whereas \(\eta\)-Se behaves as an antiferroelectric (AFE). \(\tau\)-Se behaves as a non-collinear ferrielectric (FiE), with FE polarization along the chain axis and AFE polarization in the out-of-plane direction. Rotating each constituent 1D chain of these quasi-2D Se allotropes changes the atomic symmetry, causing a change in the electrical properties. As for \(\alpha\)-Se and \(\delta\)-Se, the in-plane polarization can be changed to the out-of-plane direction. At specific rotation angles, \(\tau\)-Se distorts to a highly symmetric structure and its FiE polarization disappears. Rotation of the constituent 1D chains in the quasi-2D allotropes also changes the band structure. We observe a modification of the fundamental band gap and a change from an indirect to a direct band gap in \(\delta\)-Se.

II. COMPUTATIONAL TECHNIQUES

Our calculations of the stability, equilibrium structure, and energy changes during structural transformations have been performed using the density functional theory.
(DFT) as implemented in the VASP [15, 16] code. We used the Perdew-Burke-Ernzerhof (PBE) [17] exchange-correlation functional, augmented by the vdW correction using the DFT-D2 approach [18] to describe the inter-chain interaction. Periodic boundary conditions have been used throughout the study, with monolayers represented by a periodic array of slabs separated by a 30 Å thick vacuum region. The calculations were performed using the projector augmented wave (PAW) method [16] and 500 eV as energy cutoff. The reciprocal space has been sampled by a fine grid [19] of $9 \times 11$ $k$-points in the 2D Brillouin zone (BZ) of $\alpha$-Se, $8 \times 8$ $k$-points in $\tau$-Se, and $5 \times 11$ $k$-points in the $\delta$-Se and $\eta$-Se structures. All geometries have been optimized using the conjugate gradient (CG) method [20], until none of the residual Hellmann-Feynman forces exceeded $10^{-2}$ eV/Å. The polarization was calculated using the standard Berry phase approach [21, 22] as implemented in the VASP code.

III. RESULTS

1. Atomic structure of quasi-2D Se allotropes and their electric polarization

One characteristic of group-VI elements is their propensity to form a variety of stable 1D structures including linear sulfur/selenium chains [23, 24] and double-helices of selenium [25]. These structures can be characterized by bond angles $\gamma$ and dihedral angles $\psi$, which are defined in Fig. 1(e). $a$-helices, shown in Fig. 1(a), consist of Se atoms connected to two neighbors with a bond angle $\gamma \approx 103^\circ$ and a dihedral angle $\psi \approx 100^\circ$, and can be found in bulk Se. Through an untwisting process, an $a$-helix can be transformed to a $c$-helix, as shown in Fig. 1(c), where $\gamma \approx 113^\circ$ and $\psi \approx 64^\circ$. By changing the dihedral angle, the $a$-helix can be transformed to a $b$- or a $d$-chain [24], as shown in Fig. 1(b) and (d). Two thirds of the bond angles in the $b$- and $d$-chains are found at $\gamma \approx 106^\circ$, the remaining one third at $\gamma \approx 103^\circ$. In the $b$-chain, one third of the dihedral angles is found at $\psi \approx 100^\circ$, and rest at $\psi \approx 90^\circ$, whereas in the $d$-chain, one third of the dihedral angles is at $\psi \approx 79^\circ$, and the rest at $\psi \approx 100^\circ$. Values close to the optimum bond angle $\gamma_{\text{opt}} \approx 106^\circ$ and the dihedral angle $\psi_{\text{opt}} \approx 83^\circ$, found earlier in unconstrained finite-length Se chains [24], explain the higher stability of the $b$ and $d$-chains in comparison to the $a$- and $c$-helices by about 17 meV/atom.

Facilitated by the multi-valence nature of Se [26], these 1D Se structures can interact among each other, resulting in the formation of quasi-2D allotropes. In parallel to the parent 1D precursor $a$-helix, $b$-chain, $c$-helix and $d$-chain, we call these quasi-2D allotropes $\alpha$-Se, $\delta$-Se [24], $\tau$-Se, and $\eta$-Se [24]. Their unit cells are rectangular, with the Bravais lattice vector $\vec{a}_1$ directed along the chain axis and $\vec{a}_2$ in the inter-chain direction, and are shown in Fig. 1(f)-1(i). The bulk Se structure may be viewed as an assembly of $\alpha$-Se monolayers. Experimentally, only an $\alpha$-Se bilayer has been synthesized successfully [27]. Numerical results for the cohesive energies and structural parame-
TABLE I. Results of our DFT-PBE-D2 calculations for the optimum bond angle $\gamma$, the dihedral angle $\psi$, and the cohesive energy $E_{coh}$ of the various Se allotropes investigated in our study.

|          | $\alpha$-helix | $b$-chain | $c$-helix | $d$-chain | $\alpha$-Se | $\delta$-Se | $\tau$-Se | $\eta$-Se |
|----------|----------------|-----------|-----------|-----------|-------------|-------------|-----------|-----------|
| $\gamma$ (degrees) | 103 | 104 | 107 | 113 | 103 | 106 | 101 | 104 | 103 | 105 | 109 | 106 | 105 |
| $\psi$ (degrees) | 100 | 101 | 91 | 64 | 79 | 100 | 99 | 103 | 98 | 103 | 43 | 78 | 77 | 99 |
| $E_{coh}$ (eV/atom) | 3.359 | 3.376 | 3.361 | 3.373 | 3.476 | 3.488 | 3.462 | 3.498 |

ers of the Se allotropes shown here are summarized in Table 1.

$E_{coh}$ values of all 1D and quasi-2D Se allotropes have been calculated using total energy differences with respect to isolated Se atoms. The dynamical stability of the four quasi-2D Se allotropes discussed in this work has been confirmed by the phonon spectra displayed in Fig. 2. As an independent proof of dynamic stability, we have performed finite-temperature molecular dynamics (MD) simulations of these systems. We have found the quasi-2D $\alpha$-Se, $\delta$-Se, and $\eta$-Se structures to be stable at $T = 300$ K, but $\tau$-Se to be stable only at the lower temperature of $T = 200$ K. Additional information about the MD simulations is presented in Section D of the Appendix.

The reason why we call these allotropes ‘quasi-2D’ and not ‘2D’ or ‘1D’ is that the inter-chain interaction within the layer is much smaller than that of covalent bonds, but still stronger than the inter-layer ‘vdW’ interaction. Our DFT calculations based on the PBE-D2 functional show that in comparison to isolated 1D structures, the quasi-2D allotropes gain $\Delta E = 117$ meV/atom in $\alpha$-Se, $\Delta E = 112$ meV/atom in $\delta$-Se, $\Delta E = 101$ meV/atom in $\tau$-Se, and $\Delta E = 125$ meV/atom in $\eta$-Se. This interaction also changes the bond angles $\gamma$ and the dihedral angles $\psi$ in each 1D subsystem of these quasi-2D allotropes. Typical changes are $\Delta \gamma$, $\Delta \psi \lessgtr 2^\circ$ in $\alpha$-Se, $\Delta \gamma \lessgtr 5^\circ$ and $\Delta \psi \lessgtr 8^\circ$ in $\delta$-Se, $\Delta \gamma \lessgtr 5^\circ$ and $\Delta \psi \lessgtr 21^\circ$ in $\tau$-Se, and $\Delta \gamma \lessgtr 2^\circ$ and $\Delta \psi \lessgtr 3^\circ$ in $\eta$-Se.

Assembly of isolated 1D structures to layers also leads to a charge redistribution that may cause polarization changes in the system. Bader charges of individual Se atoms, which were all the same in isolated chains, change by $\Delta Q \approx 0.05 e$ in $\alpha$-Se, $\Delta Q \approx 0.02 e$ in $\tau$-Se, $\Delta Q \approx 0.04 e$ in $\delta$-Se, and $\Delta Q \approx 0.05 e$ in $\eta$-Se. Such charge transfers are a signature of forming local electric dipoles. Judging from Fig. 3(a)-(d), we can clearly see a depletion of the electron density in the space in-between the chains and charge redistribution among the inequivalent Se atoms. A similar change in the charge density has been reported in bilayer phosphorene [28], where $\approx 0.075 e$ per P atom have been redistributed in comparison to a superposition to monolayer charge densities, which would not be expected in a purely vdW-bonded system.

Ferroelectricity in well-studied 3D systems such as BaTiO$_3$ [9, 10] and PbTiO$_3$ [11, 12] is associated with the relative displacement of sublattices, which is characterized by the position of a representative atom within the unit cell. In the most symmetric, but least stable geometry, which we may call $B_3$, and which places this atom in the center of the unit cell, makes the system a paraelectric (PE) with no local dipole moments. Displacing this atom from the unstable $B_3$ state along a favorite direction to the most stable geometry $A$ results in an en-

FIG. 2. Phonon spectra of quasi-2D (a) $\alpha$-Se, (b) $\delta$-Se, (c) $\tau$-Se and (d) $\eta$-Se.

FIG. 3. Charge redistribution caused by connecting isolated 1D Se chains to quasi-2D (a) $\alpha$-Se, (b) $\delta$-Se, (c) $\eta$-Se, and (d) $\tau$-Se structures.
energy gain and formation of local electric dipoles causing FE behavior. Displacing the atom in the opposite direction to an equivalent geometry A' only flips the direction of the polarization by 180°.

The situation in our study is much more complex. We deal not only with one atom within a unit cell, but with many atoms in a chain segment that has an axial rotation degree of freedom. Also the calculation of the polarization using the Berry phase approach is more complex than in the above 3D systems and is presented in detail in Appendix A.

Our calculations indicate that α-Se and δ-Se are ferroelectrics with the polarization values $P = 2.53$ pC/cm in α-Se and $P = 2.96$ pC/cm in δ-Se. These values are comparable to values observed in typical 2D monochalcogenide ferroelectrics of group IV elements [29–31], such as GeS, SnS or SnSe. In τ-Se, a net electric polarization of $P_{\tau} = 0.07$ pC/cm points along the $\hat{a}_1$ direction. In the following, we will not discuss τ-Se with an AFE behavior and a vanishing net polarization, but will focus on α-Se, δ-Se and τ-Se with a non-vanishing polarization.

Within the chalcogen group, tellurium (Te) should be similar to Se not only in its chemical behavior, but also in its electronic properties. As could be expected, results published for β-Te indicate that this 2D allotrope displays about half the polarization found in Se, since systems containing this heavier element are more metallic [32].

Even though the inter-chain interaction in the 2D systems discussed here is stronger than a pure vdW interaction, it is weaker than a covalent interaction, thus allowing this rotational degree of freedom to be activated at moderate energy cost. We may thus expect gradual changes in the magnitude and direction of the polarization when activating the axial rotation degree of freedom.

2. Tunability of the polarization by chain rotation

Unlike in uniform, traditional 2D materials, where all atoms are connected by strong chemical bonds of typically ≥1 eV/atom, the quasi-2D allotropes of Se we consider here consist of 1D chains bonded by a weaker interchain interaction of around 0.1 eV/atom. This weaker interaction does not restrict the rotation of individual constituent chains. Whereas in-plane strain, applied to a general 2D system, changes the atomic structure, it usually maintains the symmetry. Rotation of the individual chains by a nonzero angle $\theta$, however, does modify the symmetry of the system. As a result, the polarization of the system, which is related to symmetry, will also be modified.

As also implied in Fig. 4(a)-4(c), the initial ground state structure A with $\theta = 0^\circ$ is equivalent to the A' structure with the same symmetry for $\theta = 60^\circ$ in α-Se, $\theta = 180^\circ$ in δ-Se, and $\theta = 20.5^\circ$ in τ-Se. The energetically degenerate structures A and A' are related to each other by a 180° rotation of the system about an axis normal to the plane. Thus, the polarization direction is reversed between A and A'.

Rotation of individual chains within the quasi-2D layer is an energetically activated process, with the barriers
related to the inter-chain interaction. For simpler systems, the transition path is usually determined using the Nudged Elastic Band (NEB) approach. Considering the number of atoms per unit cell, each with 3 degrees of freedom, and the possibility of Bravais lattice vector changes, optimizations would have to be performed in a roughly 20-dimensional configuration space, well beyond the scope of NEB. To be tractable, we make specific assumptions about the path in configuration space in an approach dubbed “poor-man’s NEB” that has been introduced previously [24]. For each rotation angle, kept as a constraint, we optimized the inter-chain distance and then the atomic positions. This approach may overshoot the value of the activation barrier at \( B_r \) between the between the ground-state structures \( A \) and \( A' \), but is still useful to characterize a likely path in configuration space involving chain rotations that leads to changes in polarization. The values of the activation barriers between equivalent configurations, determined in this way, are 60 meV/atom for \( \alpha \)-Se, 50 meV/atom for \( \delta \)-Se, and 20 meV/atom for \( \tau \)-Se, as shown in Fig. 4(d)-4(f).

We validated our approach by calculating the phonon spectra at the unstable transition structure \( B_r \) and present our results in Fig. 5. As expected, we observe a soft mode with an imaginary frequency that is characterized at \( \Gamma \) by the rotation of the constituent 1D chains towards the more stable \( A \) or \( A' \) structures in \( \alpha-B_r \), \( \delta-B_r \), and \( \tau-B_r \).

During the chain rotation from state \( A \) to \( A' \), significant changes occur in the electronic structure and especially the polarization. Our results indicate that both out-of-plane and in-plane polarization components are changing, with the polarization direction depicted in Fig. 4(a)-4(c) and the value of the in-plane component of the polarization shown in Fig. 4(d)-4(f).

An independent Bader charge calculation indicates that polarization changes are caused by charge reorganization during the rotation of individual chains. We have found that rotation of \( a \)-chains in \( \alpha \)-Se changes Bader charges on individual atoms by \( \Delta Q \approx 0.01e \). According to Fig. 4(a), changing the rotation angle from geometry \( A \) with \( \theta = 0^\circ \) to geometry \( A' \) with \( \theta = 60^\circ \) flips the direction of the in-plane polarization. At the transition state \( B_r \) with \( \theta = 30^\circ \), the polarization direction changes to out-of-plane with a value of \( P = 0.02 \) pC/cm. A similar change in polarization occurs in \( \delta \)-Se according to Fig. 4(b) during a rotation by \( \Delta \theta = 180^\circ \). For this system, \( \Delta Q \approx 0.03e \), and the transition state \( B_r \) at \( \theta = 90^\circ \) acquires an out-of-plane polarization of \( P = 0.017 \) pC/cm. According to Fig. 4(c), the behavior of \( \tau \)-Se during the rotation of the constituent \( \epsilon \)-helices is quite different. Unlike in the previous cases, the in-plane polarization direction is along and not normal to the chains, but still flips its direction during a rotation by \( \Delta \theta = 20.54^\circ \). At the activation barrier state \( B_r \) with \( \theta = 10.27^\circ \), the system turns into a highly symmetric paraelectric with a vanishing polarization.

![FIG. 5. Phonon spectra of the transition state structure \( B_r \), which is unstable with respect to the rotation of constituent chains in (a) \( \alpha \)-Se, (b) \( \delta \)-Se and (c) \( \tau \)-Se. The lowest branch of the phonon spectra with imaginary frequency is highlighted by the red line. Corresponding modes, initiating structural change, are indicated by the red arrows in the bottom panels.](image-url)
3. Tunability of the band structure by chain rotation

Not only the net polarization, but also the band structure of the system is affected by the chain rotation. Results of our DFT-PBE calculations, presented in Fig. 6(a)-6(c), suggest that all Se allotropes discussed here are semiconductors with fundamental band gaps of 1.70 eV in α-Se, 1.99 eV in δ-Se, and 1.38 eV in τ-Se. We have repeated these calculations by specifically considering the effect of spin-orbit coupling (SOC). Since the results with and without SOC, presented in Fig. 6, are very similar, we conclude that the role of SOC is not significant in our systems. Whereas the band gap values are typically underestimated in DFT calculations, the band dispersion is expected to be correct. Even though the systems are strongly anisotropic, the band dispersion along the Γ – X direction along the quasi-1D chains is not significantly smaller than along the Γ – Y direction normal to it. We expect α-Se and δ-Se to be indirect-gap semiconductors, whereas τ-Se should have a direct band gap at the Γ point. In α-Se, rotating the individual α-helices by 30° reduces the fundamental band gap to 1.40 eV and turns it into a direct gap near the S-point, as seen in Fig. 6(d). As seen in Fig. 6(e), a 90° rotation of the δ-chains in δ-Se causes a reduction of the band gap to 1.55 eV, but keeps the gap indirect. According to Fig. 6(f), the band gap in τ-Se remains indirect, but is reduced to 0.80 eV as the τ-helices rotate by 10.27°.

4. Effect of in-plane strain on the polarization of quasi-2D Se allotropes

We also study the effect of in-plane uniaxial strain on the polarization. To do so, we strain the lattice uniformly along the ̂a_1 direction, which is aligned with the axes of the constituent chains in α-Se, δ-Se and τ-Se. To reproduce the realistic response of a system subject to this strain, we allow the a_2 lattice constant to relax for each value of a_1. As the quasi-2D structures are stretched along the ̂a_1 direction, they shrink linearly along the ̂a_2 direction, indicating a positive Poisson ratio.

For α-Se shown in Fig. 7(a) and δ-Se in Fig. 7(b), the change in the lattice constant a_2 is about one fourth of the change in the lattice constant a_1 along the chain axis. The resulting Poisson ratios are ν≈0.22 for α-Se and ν≈0.27 for δ-Se. According to Fig. 7(c), the Poisson ratio of τ-Se, ν≈0.54, is about twice that of δ-Se.

The net polarization as a function of strain is also shown in Fig. 7(a)-7(c). These results indicate a linear increase in the polarization as the structure is compressed along the chain axis. For the uniaxial strain value σ_x=−4%, we observe an increase in the polarization by 9.8% in α-Se, 9.1% in δ-Se, and by 37.5% in τ-Se.

As can be inferred from Fig. 1(a) and 1(c), the α-helix component of α-Se and the τ-helix component of τ-Se are topologically related. They can be transformed from one to another by a twisting/untwisting process, in which the bond angles and the dihedral angles change. We should note that for supercells containing the same number of atoms, the lattice constant along the chain direction is a = 4a_1 for α-Se and a = 3a_1 for τ-Se. The energy change ΔE as a function of the supercell length in these two allotropes is shown in Fig. 7(d). We set the optimum structure of the more stable α-Se allotrope as the energy reference, with the optimum τ-Se structure being less stable by only 15 meV/atom. At the supercell lattice constant a = 18.72 Å, the energy of stretched τ-Se equals that of compressed α-Se, indicating the possibility of a strain-induced phase transformation at this point.

5. Effect of in-plane strain on the band structure of quasi-2D Se allotropes

We also study the effect of in-plane uniaxial strain on the band structure of α-Se, δ-Se and τ-Se. Our results, presented in Fig. 8, indicate that the three allotropes keep their semiconducting character when the quasi-1D structures are axially compressed or stretched, with strain values σ_x ranging from −4% to +4%. Similar to our results for unstained systems in Fig. 6, α-Se and δ-Se remain indirect-gap semiconductors, whereas τ-Se has a direct band gap at the Γ point independent of strain. We find that the fundamental band gap widens under compression and shrinks in stretched systems. In particular, under σ_x=−4% compression, E_g increases by 14% in α-Se, 3.3% in δ-Se and 3.6% in τ-Se. Under σ_x=+4% stretch,
$E_g$ decreases by 20% in $\alpha$-Se, 5.4% in $\delta$-Se and 2.5% in $\tau$-Se. This behavior does not follow the naive picture for 1D systems that stretching elongates bonds, thus reducing hopping and the bandwidth, leading to wider band gaps. In the quasi-2D systems we study, stretching the chains reduces the inter-chain distance and thus increases the inter-chain interaction. Since the band dispersion along and normal to the chain direction is comparable, the naive picture of 1D systems no longer applies, resulting in dispersion changes seen in Fig. 8.

IV. DISCUSSION

We studied the possibility to tune the electric polarization of four quasi-2D allotropes of Se. Besides $\alpha$-Se, the naturally occurring phase consisting of $a$-helices, we also studied $\delta$-Se, $\eta$-Se and $\tau$-Se, which differ only in their dihedral angles and should be similarly stable. The transformation of the $a$-helix to a $b$-chain, the constituent of $\delta$-Se, has been discussed earlier [24]. A change of the dihedral angle leads to the $d$-chain of $\eta$-Se, and untwisting the $a$-helix leads to the $c$-helix of $\tau$-Se. Interaction of these 1D structures should, as in the case of $\alpha$-Se, lead to the formation of corresponding quasi-2D structures. Since the unit cells of these four allotropes are very different, selecting a suitable substrate with a matching lattice constant should cause preferential epitaxial growth of a given allotrope. Charge redistribution due to the inter-chain interaction causes a net electric polarization in many of these quasi-2D allotropes.

Our calculations of the polarization behavior in these unusual systems are performed using a well-established approach [32], where we first identify a related, highly symmetric paraelectric structure with no local dipoles, which we call $B_S$. For the sake of completeness, we provide specific details about the construction of the $B_S$ state in Appendix A. The nature of the polarization behavior is then deduced by comparing the charge distribution in a given system to that in the $B_S$ state.

Changes of the electric polarization in ferroelectrics are caused by relative displacement of sublattices. In most common ferroelectrics including BaTiO$_3$, the interaction among atoms forming such sublattices is indirect, effectuated by strong covalent or ionic bonds to atomic neighbors in other sublattices. In absence of a hierarchy of weaker and stronger interactions in the system, a selective mechanical displacement of a sublattice appears...
impossible.

The situation is very different in quasi-2D Se allotropes discussed here, which consist of covalently bonded 1D constituents that form sublattices. The weaker interaction between the 1D systems provides one additional degree of freedom, namely the axial rotation. This rotation, as we have shown, may change not only the magnitude, but also the direction of the polarization from in-plane to out-of-plane. We can imagine two scenarios to effectuate such a rotation.

One of these scenarios uses nano-sized combs that have been synthesized recently [33, 34]. We can imagine a comb structure pressing from top onto a quasi-2D Se structure adsorbed on a substrate. Inserting the ‘teeth’ of the comb in-between the chains and moving them along the chain direction should result in a torque that would rotate each chain. The other scenario is to place the quasi-2D system within a planar interface in-between two solid blocks in a sandwich configuration. Applying in-plane shear while pressing the blocks together should cause the quasi-1D components to rotate like tree logs on a wagon. In both cases, we estimate that a torque $> 10^{-20}$ Nm per unit cell should be required to initiate the rotation of chains. Strain transfer to the quasi-2D allotropes will be most efficient when using solid blocks with a high Young’s modulus such as polydimethylsiloxane or polyvinyl alcohol [35, 36].

We also imagine two scenarios to flip the direction of the polarization in our quasi-2D Se allotropes. Both scenarios involve atomic motion across a barrier in an energetically activated process. In the first scenario, which involves a higher activation energy and is discussed in more detail in Appendix C, atoms in a rigid unit cell are displaced in opposite directions from the initial state A, across a highly symmetric transition state $B_S$, to the final state $A'$ with the same energy as A. This process is shown in Fig. 11(a)-11(c). Since the bond lengths and bond angles change significantly during this process, the energy cost is rather high, amounting to 80.1 meV/atom in $\alpha$-Se, 106.4 meV/atom in $\delta$-Se, and 40.3 meV/atom in $\tau$-Se according to Fig. 11(d)-11(f).

The second scenario involves a special rotation of the constituent 1D structures in the quasi-2D Se system, as illustrated in Fig. 4. In comparison to the first scenario, the energy investment here is lowered to about 69.7% for $\alpha$-Se, 42.5% for $\delta$-Se, and 45.1% for $\tau$-Se of its initial value. Thus, we may expect that applying an external electric field may cause an axial rotation of rigid 1D structures rather than atomic displacement within a rigid unit cell. Clearly, lowering the inter-chain interaction should lower the energy cost, allowing the chains to rotate more easily. On the other hand, the inter-chain interaction must be significant enough to cause charge redistribution and lead to polarization. We believe that the quasi-2D Se allotropes discussed here bring a good balance of both effects, providing the possibility to tune the polarization by allowing for structural changes at a very moderate energy cost.

The high flexibility of 1D Se chains in terms of bond length, bond angle and dihedral angle suggests that many more structures beyond the four allotropes discussed here may be realized, resulting in other quasi-2D structures with very different electronic properties.

V. SUMMARY AND CONCLUSIONS

In summary, we have performed ab initio DFT calculations to study the polarization and band structure of four quasi-2D allotropes of Se, which we called $\alpha$-Se, $\delta$-Se, $\eta$-Se and $\tau$-Se. These allotropes are formed from their one-dimensional (1D) constituents, which we call the a-helix, b-chain, c-helix and d-chain, and which possess a rotational degree of freedom about their axis. The inter-chain interaction is not strong enough to suppress the rotation of these chains, but still causes a charge redistribution within the quasi-2D structures that results in a net polarization. $\alpha$-Se and $\delta$-Se display an FE behavior with an in-plane polarization, directed normal to the 1D chains. An in-plane polarization also occurs in $\eta$-Se, which displays an AFE behavior. $\tau$-Se behaves as a non-collinear ferrielectric, with FE polarization along the chain axis and AFE polarization in the out-of-plane direction. Rotating each constituent 1D chain in these quasi-2D Se allotropes changes the atomic symmetry and also the electronic structure. In the $\alpha$ and $\delta$ allotropes, chain rotation changes the polarization direction from in-plane to out-of-plane. At specific rotation angles, $\tau$-Se distorts to a highly symmetric structure and its FiE polarization disappears. Along with changes in polarization, caused by chain rotation, come changes in the electronic band structure of these semiconducting allotropes including a modification of the fundamental band gap, which may change from an indirect to a direct gap in $\delta$-Se. In-plane strain along the axial direction of the 1D structures only modifies the magnitude of the polarization.

APPENDIX

A. Polarization calculation using the Berry phase approach

Polarization studies of a given allotrope using the Berry phase approach begin with the construction of a highly symmetric PE counterpart of this allotrope with no local electric dipoles. Specifics of the construction process are outlined in Appendix B. For the allotropes in this study, we display the morphology of the PE state, characterized by the symbol $B_S$, in Fig. 9, and determine their charge distribution. Structural optimization of the $B_S$ state in these allotropes causes a a reduction of the space group symmetry from $P2_1m$ to $P2$ in $\alpha$-Se, from $Pnma$ to $Pma2$ in $\delta$-Se, and from $Pnma$ to $P2_1$ in $\eta$-Se. This essentially translates to loss of mirror symmetry with respect to a plane normal to the inter-chain
Comparing the charge difference between these quasi-2D allotropes and their corresponding \( B_S \) states, we observe an parallel electrical polarization along the \( \vec{a}_2 \) direction of \( \alpha \)-Se and \( \delta \)-Se indicating FE behavior, shown in Fig. 9(e) and (f). And an antiparallel electrical polarization along the \( \vec{a}_2 \) direction of \( \eta \)-Se indicating an AFE behavior, shown in Fig. 9(h). A special behavior occurs in the unit cell of \( \tau \)-Se. In comparison to the \( B_S \) structure, two positively charged atoms both move in the same direction along \( \vec{a}_1 \), but in opposite directions normal to the plane. The space group symmetry \( P222_1 \) reduces to \( P2_1 \) in \( \tau \)-Se, as the rotation symmetry about \( \vec{a}_2 \) and about the direction normal to the layer in the \( B_S \) structure is lost, with only the rotation symmetry about \( \vec{a}_1 \) remaining. As a result, \( \tau \)-Se displays a non-collinear polarization behavior, indicated in Fig. 9(g). We use the term ‘FIE’, which is defined for the similar non-collinear polarization in a \( \delta \)-GeS monolayer \[31\], to describe the polarization behavior in \( \tau \)-Se. The polarization of the quasi-2D Se allotropes discussed here is shown by the red arrows in Fig. 1(f)-1(i).

B. Construction and characterization of the PE state in quasi-2D Se allotropes

We use a traditional approach to construct the highly symmetric paraelectric state called \( B_S \). We start from the initial structure \( A \) and identify the polarization direction. We reflect \( A \) about a mirror plane that is perpendicular to the polarization direction to arrive at \( A' \). Since \( A \) and \( A' \) are mirror symmetric, the polarization of \( A' \) is opposite to that of \( A \). A state mid-way between \( A \) and \( A' \) has zero polarization and is identified as the paraelectric reference state \( B_S \). As can be seen in Fig. 9, such paraelectric structures have a higher symmetry in comparison to the initial state \( A \) shown in Fig. 1.

We calculate the phonon spectra of these paraelectric structures \( B_S \) and show the results in Fig. 10. The phonon mode associated with the largest imaginary frequency at the \( \Gamma \)-point indicates a decay to more stable structures \( A \) and \( A' \).
C. Flipping the polarization by atom displacement

One possible way to flip the polarization direction in the quasi-2D allotropes by 180° is to displace specific atoms within the unit cell in a particular way. Let us focus on α-Se, δ-Se and τ-Se with a nonzero polarization. Starting from the initial state, we displace specific atoms along the direction indicated by the red arrows in Fig. 11. The displacement continues across the barrier state $B_S$ shown in Fig. 9 and completes at the state $A'$. The stability of $A$ and $A'$ is the same, but the polarization is opposite. The atomic displacement process causing a flip of the polarization direction is shown in Fig. 11(a) for α-Se, Fig. 11(b) for δ-Se, and Fig. 11(c) for τ-Se. The energy barrier in this process is $\Delta E \approx 80.08$ meV/atom for α-Se, $\Delta E \approx 106.41$ meV/atom for δ-Se, and $\Delta E \approx 40.3$ meV/atom for τ-Se, as seen in Fig. 11(d)-11(f). The gradual change of polarization caused by atom displacement is shown by the red dashed lines in Fig. 11(d)-11(f). Starting from the most stable state $A$, the polarization first decreases to zero at the paraelectric reference state $B_s$, and then increases to the initial value with opposite direction at the final state $A'$.  

D. Finite-temperature MD simulations of quasi-2D Se structures

We have performed canonical MD simulations at finite temperatures as an independent proof of the thermodynamical stability of the quasi-2D α-Se, η-Se and τ-Se structures described in the main text. Results of 2 ps long runs at $T = 300$ K are shown in Video 1 for α-Se and Video 2 for η-Se. Results of a 2 ps run for δ-Se at $T = 300$ K were published earlier [24]. As can be inferred from Figs. 4 and 11, the energy barrier in τ-Se is much smaller than in α-Se and δ-Se. We have also found τ-Se to become unstable at 300 K. Therefore, we present results of a 2 ps run for τ-Se in Video 3 at a lower temperature $T = 200$ K.

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