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Structural phase transition and material properties of few-layer monochalcogenides

Mehrdad Mehboudi,1 Benjamin M. Fregoso,2 Yurong Yang,1 Wenjuan Zhu,3 Arend van der Zande,4 Jaime Ferrer,5 L. Bellaiche,1 Pradeep Kumar,1 and Salvador Barraza-Lopez1,*

1Department of Physics, University of Arkansas, Fayetteville, AR 72701, USA
2Department of Physics, University of California, Berkeley, CA, 94720, USA
3Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
4Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
5Departamento de Fisica, Universidad de Oviedo, Asturias, Spain
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GeSe and SnSe monochalcogenide monolayers and bilayers undergo a two-dimensional phase transition from a rectangular unit cell to a square unit cell at a temperature $T_c$ well below the melting point. Its consequences on material properties are studied within the framework of Car-Parrinello molecular dynamics and density-functional theory. No in-gap states develop as the structural transition takes place, so that these phase-change materials remain semiconducting below and above $T_c$. As the in-plane lattice transforms from a rectangle onto a square at $T_c$, the electronic, spin, optical, and piezo-electric properties dramatically depart from earlier predictions. Indeed, the $Y$– and $X$–points in the Brillouin zone become effectively equivalent at $T_c$, leading to a symmetric electronic structure. The spin polarization at the conduction valley edge vanishes, and the hole conductivity must display an anomalous thermal increase at $T_c$. The linear optical absorption band edge must change its polarization as well, making this structural and electronic evolution verifiable by optical means. Much excitement has been drawn by theoretical predictions of giant piezo-electricity and ferroelectricity in these materials, and we estimate a pyroelectric response of about $3 \times 10^{-12} \text{C/Km}$ here. These results uncover the fundamental role of temperature as a control knob for the physical properties of few-layer group-IV monochalcogenides.

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Few-layer group-IV monochalcogenides are semiconductors [1–7] with a structure similar to that of black phosphorus that exhibit a giant piezoelectric response in monolayer (ML) samples according to theory [5, 8]. The four-fold degeneracy of their structural ground state first predicted by us in the past [9] leads to ferroelectricity [9–11]. These materials bring the concept of two-dimensional (2D) valleytronics on materials with reduced structural symmetries [12] closer to reality too [13]. Ferroelectrics must also exhibit a pyroelectric response, yet no theoretical description of this process has been provided for these 2D materials as of now.

It remains unknown whether these materials undergo a complete degradation when exposed to air at the few-layer limit. Nevertheless, theory tells us that these monolayers host two-dimensional piezoelectricity, ferroelectricity, and a valley physics that is addressable with linearly-polarized light. Previous qualities do not exist simultaneously in any other known 2D atomic phase and justify additional theoretical and experimental studies. Adding to this list of properties, here we show that a structural transition taking place at finite temperature ($T$) modifies their band structure and hence their hole transport and optical properties, and induces a pyroelectric response. Realizing these host of theoretical predictions requires thermally-controllable experimental studies of few-layer monochalcogenides in an inert atmosphere.

Theoretical results based on density-functional theory in Refs. [1–7, 10, 11, 13] correspond to structures at $T = 0$ K displayed in Fig. 1(a), and belong at the far left on the structure vs. $T$ plots in Fig. 1(c) and 1(d). We performed Car-Parrinello molecular dynamics (MD) calculations at finite $T$ [14–18] on $8 \times 8$ ML and AB-stacked bilayer (BL) supercells containing up to 512 atoms, with pseudopotentials and basis sets carefully validated [19], that led to the structural evolution at finite $T$ presented in Fig. 1(c-f). In order to focus on the results, thorough descriptions of methods, as well as the full time-evolution of the instantaneous $T$, total energy $E$, in-plane strain, and order parameters at selected target temperatures are provided as Supplemental Material (SM, Section I).

In Fig. 1(a) we illustrate a 2D structural transition whereby a rectangular unit cell with three-fold coordinated atoms at $T < T_c$ turns onto a square unit cell with five-fold coordinated atoms at $T \geq T_c$. The transition is captured in Fig. 1(c-f) by the thermal evolution of structural order parameters shown in Fig. 1(b) that include (i) lattice constants $a_1$ and $a_2$, obtained in four (eight) inequivalent ways in MLs (BLs) at any given unit cell, (ii) interatomic distances up to third nearest neighbors ($d_1$, $d_2$ and $d_3$), and (iii) angles subtended among a given atom and its second-nearest neighbors ($\alpha_3$), third-nearest neighbors ($\alpha_1$) and second- and third-nearest neighbor ($\alpha_2$).
The time auto-correlation of order parameters $a_1$ and $a_2$—a measure of the time scale of structural fluctuations—vanishes within 800 fs (Fig. 5, SM). Ensemble averages obtained from trajectories over 15,000 fs after thermal equilibration are reported in Figs. 1(c-f) for $\langle a_1 \rangle$, $\langle a_2 \rangle$, $\langle d_1 \rangle$, and $\langle \alpha_i \rangle$ ($i = 1,3$).

Sudden changes of structural order parameters signal the transition temperature $T_c$. For example, $\langle a_1 \rangle/\langle a_2 \rangle > 1$ at $T = 0$ K. The transition is signaled by $\langle a_1 \rangle/\langle a_2 \rangle = 1$. This ratio of lattice parameters decreases with increasing atomic number, so that SnSe MLs are expected to have a smaller $T_c$ than GeSe MLs [9]. Additional signatures of the transition are the coalescence of $d_2$ and $d_3$ onto a single value, and the coalescence of in-plane angles defined in Fig. 1(b) toward $90^\circ$. As seen in Fig. 1, the transition occurs at $T_c = 300 \pm 17$ K for GeSe MLs and at a higher temperature of $350 \pm 16$ K for GeSe MLs. It is interesting to note that the square unit cell—corresponding to a point of unstable equilibrium at $T = 0$ K [9, 20]—becomes, on average, the preferred structure at $T_c$.

Now, $\langle a_1 \rangle/\langle a_2 \rangle$ is known to increase with the number of layers for a given layered monochalcogenide as well [4] and, accordingly, one should expect an increase of $T_c$ for a given material in going from MLs to BLs. Within the temperature resolution of 25 K employed in our calculations, we see a 50 K increase of $T_c$ in going from MLs to BLs. Such increase makes our results consistent with experiments on bulk SnSe, where $T_c$ is of the order of 800 K [20–23] (MD simulations of bulk samples require inclusion of four monolayers and are out of our reach). The structural change discussed on this and previous paragraph should be experimentally observable with XRD techniques.

We note that a melting transition would be signaled by an isotropic increase of interatomic distances $\langle d_1 \rangle$, $\langle d_2 \rangle$ and $\langle d_3 \rangle$. But the mean (inter-sublayer) distance...
Electron energy (eV) obtained on instantaneous supercells at times transition: the electronic density of states (DOS) shows a well-defined bandgap for a finite probability with increasing temperature, and a nature of atomistic fluctuations (disorder). Excursions of t out of one hundred and fifty individual frames at times order parameter. Considering these fluctuations, material properties to be discussed next were evenly sampled out of one hundred and fifty individual frames at times \( t_i = 5000 + 100i \) fs \((i = 1, 2, 3, \ldots, 150)\).

These materials remain semiconducting through the transition: the electronic density of states (DOS) obtained on instantaneous supercells at times \( t_i \) in Fig. 2 shows a well-defined bandgap for \( T \) below and above \( T_c \) (details of DOS calculations are disclosed in SM). The bandgaps in Fig. 2—which are visible in Table I (SM)—change by about 200 meV at 400 K with respect to their values at 0 K. The DOS has two additional features: (i) sharpest peaks at 0 K that become blurred at increasing \( T \) and (ii) shallow DOS pockets around the valence-band maximum for \( T < T_c \) that are emphasized by yellow (gray) rectangles extending onto band structure subplots to the right.

Band structures in Fig. 2 were obtained from instantaneous unit cells built from average lattice and basis vectors at times \( t_i \) defined above. The width of these bands is another experimentally-observable indicator of structural fluctuations that must be visible on ARPES data. The sharp peaks in the DOS at 0 K correspond to relatively flat bands located around the \( \Gamma \) point whose energy location fluctuates with increasing \( T \), thus making these peaks shallower. A band unfolding scheme [25–28] confirms these findings.

2D materials with reduced structural symmetries originate a novel paradigm in valleytronics in which crystal momentum labels individual valleys one-to-one [12]. In SnSe and GeSe MLs and BLs, the shallow DOS pocket at 0 K \( \langle \alpha_1 \rangle > \langle \alpha_2 \rangle \) corresponds with a hole-valley \((h, 2)\) located along the \( \Gamma \)–\( X \) line in Fig. 2 [1, 2, 4] that lies at a higher energy when contrasted to the hole-valley at the \( \Gamma \)–\( Y \) line \((h, 1)\).

Band structure insets in Fig. 2 show the effect of \( T \) on valley spin polarization that arises due to spin-orbit coupling (SOC) [29]. The spin-polarization at these insets becomes drastically degraded at \( T_c \) because spin-up (solid black) and spin-down (dashed yellow) bands become broader and closer together. For this reason, the remaining results on this Letter will neglect the effect of

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**FIG. 2.** (Color online.) Electronic DOS and band structures for \( t_i = 1500 + 100i \) fs \((i = 1, 2, 3, \ldots, 150)\) for (a) GeSe ML, (b) GeSe BL, (c) SnSe ML, and (d) SnSe BL at 0, 200, and 400 K. The DOS and band structures become broader with increasing \( T \), but no in-gap states are seen in the DOS nor the band structures despite of fluctuations. The \( X \)– and \( Y \)– points are inequivalent for \( T < T_c \) and become equivalent for \( T \geq T_c \) as \( \alpha_1 = \alpha_2 \). The zero energy was set at the mid-gap. The thermal dependence of the hole conductivity should display an anomalous behavior at \( T_c \) when valleys 1, \( h \) and 2, \( h \) align.
SOC. (AB BLs have zero spin polarizations at individual valleys due to inversion symmetry.)

As shown thus far, MLs and BLs increase their structural symmetry as $T_c$ is approached from below (Fig. 1). This means that the $X$- and $Y$-points in reciprocal space—which were inequivalent for $T < T_c$—become equivalent for $T \geq T_c$ as $(\alpha_1) = (\alpha_2)$. As $T_c$ is reached, the hole valley along the $\Gamma - Y$ direction raises up to align with the valley located along the $\Gamma - X$ line (Fig. 2). One valley contributes to the hole conductivity at the band edge for $T < T_c$, while two valleys contribute at $T \geq T_c$, giving rise to an anomalous thermal dependence of the hole conductivity at $T = T_c$ that should be visible in standard transport measurements of gated or hole-doped samples.

As seen in Fig. 3(a), crystal momentum couples to the orientation of adsorbed linearly polarized light [13]. But the induced equivalence among the $X$- and $Y$-points for $T \geq T_c$ makes the optical adsorption band edges for horizontally- and vertically-polarized light identical, making the band edge becomes polarized at $45^\circ$, which then represents an additional optical signature of the structural transition.

The binary composition of MLs and the asymmetry upon inversion about an axis parallel to $a_2$ originates a net electric dipole $p$ along the longest lattice vector ($a_1$) [3], resulting in a piezoelectric response at 0 K [5, 8]. But as $\alpha_1$, $\alpha_2$, and $\alpha_3$ fluctuate (Fig. 1(b-e)), the orientation of these dipoles randomizes at $T_c$, turning the net electric dipole moment to zero. This hypothesis is demonstrated in Fig. 3(b) by averaging the mean electric dipole moment to zero. This hypothesis is demonstrated in Fig. 3(b) by averaging the mean electric dipole moment to zero over times $t_i$ at a given $T$ on instantaneous average unit cells (section VI, SM).

The three salient features of ferroelectrics are: (i) piezoelectricity, (ii) ferroelectricity, and (iii) pyroelectricity. The abrupt decay of $p$ around $T_c$ was fitted to sigmoidal functions, whose temperature derivative $dp/dT$ is the pyroelectric response given at lower subplots in Fig. 3(b). The pyroelectricity hereby predicted may very well be a first within the field of 2D atomic materials.

To conclude, we predict a structural transition in MLs and AB BLs of GeSe and SnSe. The transitions should be observable on mean values of lattice parameters and (in-plane) distances and angles among second and third nearest neighbors (XRD). These materials remain semiconductors through the transition, which should also be observable through ARPES, hole conductivity, and optical absorption measurements. We contributed the pyroelectric response of GeSe and SnSe MLs as well. These theoretical results may motivate and guide future experimental work in these few-layer materials with detailed thermal control and performed on an inert atmosphere.

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* sbarraza@uark.edu

mat.mes-hall].


