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Normal-to-topological insulator martensitic phase transition in group-IV monochalcogenides driven by light

Jian Zhou¹, Shunhong Zhang² and Ju Li³

Abstract

A material potentially exhibiting multiple crystalline phases with distinct optoelectronic properties can serve as a phase-change memory material. The sensitivity and kinetics can be enhanced when the two competing phases have large electronic structure contrast and the phase change process is diffusionless and martensitic. In this work, we theoretically and computationally illustrate that such a phase transition could occur in the group-IV monochalcogenide SnSe compound, which can exist in the quantum topologically trivial *Pnma*-SnSe and nontrivial *Fm $\bar{3}m$* -SnSe phases. Furthermore, owing to the electronic band structure differences of these phases, a large contrast in the optical responses in the THz region is revealed. According to the thermodynamic theory for a driven dielectric medium, optomechanical control to trigger a topological phase transition using a linearly polarized laser with selected frequency, power and pulse duration is proposed. We further estimate the critical optical electric field to drive a barrierless transition that can occur on the picosecond timescale. This light actuation strategy does not require fabrication of mechanical contacts or electrical leads and only requires transparency. We predict that an optically driven phase transition accompanied by a large entropy difference can be used in an “optocaloric” cooling device.

Introduction

Phase change memory (PCM) materials are one of the key components of next-generation information storage¹. Currently, the most widely used commercialized PCM materials are Ge–Sb–Te alloys². These materials can exist in both crystalline and amorphous phases with distinct optical or electronic transport features, which are separated by a significant energy barrier. The phase transformation between these phases is reconstructive owing to the diffusional displacements of atoms. The drawback of a temperature-driven transformation is that due to the

equipartition theorem, all phonon modes are involved, and thus, the total driving energy and the heat dissipation are significant. Furthermore, the phase change occurs on a timescale on the order of a few to a few hundred nanoseconds. Hence, one would like to find a PCM material that can simultaneously satisfy the following requirements: (i) it can exist in at least two structural phases, (ii) these phases have distinct physical properties that can be easily measured, preferably in a contact-free manner, (iii) the phase transformation is displacive/martensitic, where the atomic motions are diffusionless, and (iv) the directed phase transition preferably occurs within a single phonon oscillation period (picosecond) in the barrier-free limit. The main idea is to strongly bias *only* the reaction coordinates of the structural transition, instead of exciting all the phonon modes, such as in a temperature-driven transition. With these requirements fulfilled, the phase transition would have the benefits of low energy consumption, low heat load and fast switching speed.

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The discovery of topological materials during the past decade has offered ample interesting physical effects³. Transitions between topologically different states have attracted tremendous attention both theoretically and experimentally. One example is group-VI transition metal dichalcogenide (TMD) monolayers, such as MoTe_2 and its analogues, which exist in the 2H (normal insulator, NI)⁴ and 1T' (topological insulator, TI) phases⁵. Theoretical predictions have shown that the 2H \rightarrow 1T' phase transformation can occur under lithiation⁶, electron doping⁷, or tensile strain⁸. Later experimental efforts showed that such a phase transformation can occur under Ar plasma bombardment⁹ or gate voltage¹⁰. During this process, $\sim 1/6$ of the Mo-Te chemical bonds need to be broken, and then, the same number of new Mo-Te bonds will be formed. Hence, even though the energy difference between 2H- MoTe_2 and 1T'- MoTe_2 is small, the energy barrier separating the two phases is high ($\sim 2000 \text{ J/cm}^3$ when we take an energy barrier of 1.05 eV/f.u. and a MoTe_2 monolayer thickness of 7.74 \AA ^{5,8}). Most other topological phase transitions in a single material occur via modulation of their electronic band dispersion under strain engineering^{11,12}, electrostatic gating^{13–15}, or temperature change^{16,17}. Some of these phases have a short lifetime (volatile) once the external field is removed. In addition, these phase transitions usually require electrochemical, electrical, or mechanical contacts and patterning. This stimulates us to explore topological phase change materials whose phase transition can be triggered through a *noncontacting* scheme with intermediate energy barriers¹⁸.

In this work, based on thermodynamic analysis and first-principles density functional theory (DFT) calculations, we propose that a group-IV monochalcogenide compound (such as SnSe or other analogues) is a good platform to realize nonvolatile topological phase transition by optomechanical stimulation. This group-IV monochalcogenide compound family possesses a few interesting properties^{19,20}. The SnSe compound can exist in multiple phases, such as in the space groups of *Pnma*, *Fm $\bar{3}m$* , and *Cmcm*. While many studies focus on the high-temperature ($> 800 \text{ K}$) phase transition from *Pnma* to *Cmcm*^{21,22}, here, we study the two energetically lower polymorphs, namely, *Pnma* (ground state) and *Fm $\bar{3}m$* (metastable). Geometrically, *Pnma*-SnSe is a layered structure. This phase has been attracting great interest owing to its good thermoelectric property^{22–24}. *Fm $\bar{3}m$* -SnSe shows a rocksalt geometry and has been proven theoretically^{25,26} and experimentally^{27,28} to be a novel type of quantum topological material – a topological crystalline insulator (TCI) with a large change in near band-edge (NBE) optical susceptibilities. Hence, the topological phase transition between *Pnma* and *Fm $\bar{3}m$* would be interesting and promising for potential

applications. Nevertheless, except for foreign atom doping^{29,30}, theoretical studies on such phase transitions are very rare. Here, we apply the random phase approximation (RPA) to calculate the optical response features. Owing to the topological band inversion feature of *Fm $\bar{3}m$* -SnSe, its dielectric screening effect is much stronger than that of semiconducting *Pnma*-SnSe. Therefore, according to the thermodynamic theory of a driven dielectric medium, when the sample is exposed to a linearly polarized laser (LPL) with THz frequency, the free energy of *Fm $\bar{3}m$* -SnSe reduces faster with greater alternating electric field strength (the optical tweezers effect) than that of *Pnma*-SnSe. Hence, we predict a phase transformation between *Pnma* and *Fm $\bar{3}m$* under an intermediate intensity LPL. Such a transformation can even be barrier-free, with significantly enhanced kinetics. Owing to the entropy difference between the two phases, we can even design a thermodynamic phase-change cycle to utilize the “optocaloric” effect of SnSe as a refrigeration medium.

Methods

Density functional theory

We employ DFT calculations^{31,32} with generalized gradient approximation (GGA)³³ treatment of the exchange-correlation energy term using the Vienna *ab initio* simulation package (VASP)^{34,35}. The projector augmented wave (PAW) method³⁶ and a planewave basis set with a cutoff energy of 300 eV are applied to treat the core and valence electrons in the system, respectively. The first Brillouin zone is represented by a Γ -point-centered Monkhorst–Pack *k*-mesh³⁷ with a grid density of $2\pi \times 0.02 \text{ \AA}^{-1}$ along each dimension. The convergence of these parameters is well tested. To correct the underestimation of long-range dispersion in the GGA treatment, we include the semiempirical quantum chemical method DFT-D3 term in the total energy expression³⁸. Other treatments give similar results. The convergence criteria of the total energy and force component are set to $1 \times 10^{-7} \text{ eV}$ and 0.001 eV/\AA , respectively. Spin-orbit coupling (SOC) is self-consistently included due to the high *Z* of Sn and Se atoms. We perform *ab initio* molecular dynamics (AIMD) simulations and confirm that both phases are thermally stable at room temperature (Fig. S1 in the Supplementary Information). To evaluate the finite temperature behavior, we also calculate phonon dispersions and the frequency density of states using the finite displacement method, as implemented in the Phonopy code³⁹.

Results and discussion

When an LPL containing an alternating electric field ($\vec{\mathcal{E}}(\omega_0, t) = \mathcal{E}_0 e^{-i\omega_0 t} \hat{\mathbf{e}}_i$, where $\hat{\mathbf{e}}_i$ is a unit vector along the *i*-th direction) is applied to the system, its contribution to

the free energy can be evaluated via the thermodynamic theory of an external reservoir bath and Legendre transformation. By taking the electric field magnitude as the thermodynamic variable, one adds an additional term into the free energy density (in units of energy/volume)⁴⁰,

$$G_E = -\frac{1}{2}\vec{\mathcal{E}}^*(\omega_0, t) \cdot \boldsymbol{\epsilon}^{(1)}(\omega_0) \cdot \vec{\mathcal{E}}(\omega_0, t). \quad (1)$$

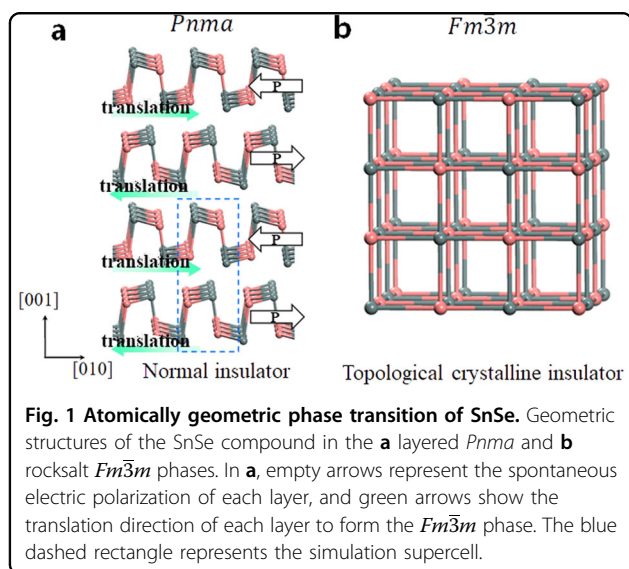
Here, $\boldsymbol{\epsilon}^{(1)}(\omega_0)$ is the real part of the dielectric function tensor at optical frequency ω_0 . Note that here, the optical frequency ω_0 is much larger than the vibrational frequency ω^{vib} (typically < 6 THz); thus, the ion motion contribution to the dielectric function is neglected. Microscopically, the incident photon carries an optical electric field and excites electron subsystems. Then, phonons are stimulated by electron-phonon coupling. When the phonon displacement is large enough, the system can go beyond elastic deformation and undergo a phase transition.

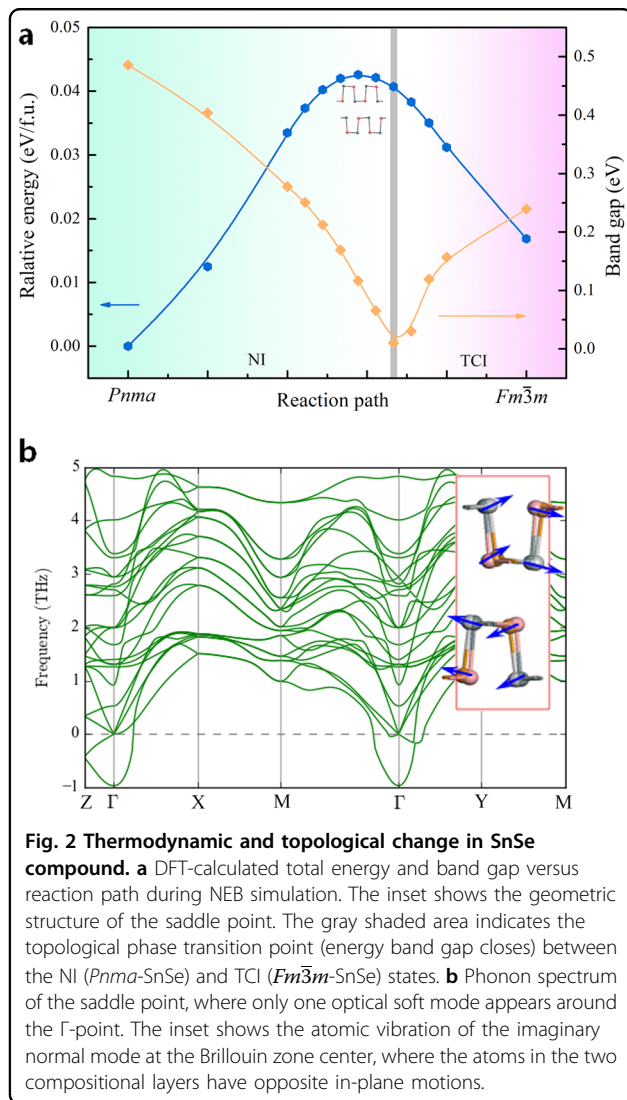
We start our discussions with the geometric and energetic features of the SnSe compound in both the *Fm* $\bar{3}$ *m* and *Pnma* phases (Fig. 1). *Pnma*-SnSe shows a layered structure. According to previous works, each SnSe layer possesses an in-plane (along the *y*-direction) ferroelectricity ($P_0 = 1.5 \times 10^{-10}$ C/m)^{41,42}. In the bulk *Pnma*-SnSe compound, the layers are antiferroelectrically stacked, exhibiting a centrosymmetric structure with no net spontaneous polarization. This structure has been demonstrated to be a semiconductor with an optical band gap of 0.9 eV, showing high-performance thermoelectric behavior ($ZT > 2.2$)^{22,23}. In contrast, in the rocksalt *Fm* $\bar{3}$ *m*-SnSe, all the Sn and Se atoms are ionically bonded. Its band dispersion calculation reveals an inverted band order near the Fermi level, which is topologically protected by spatial mirror symmetry²⁵. Thus, this structure

belongs to the TCI family, with a calculated band gap of ~ 0.2 eV⁴³. Our DFT-D3 scheme yields *Pnma*-SnSe lattice parameters of $a = 4.169$ Å, $b = 4.515$ Å, and $c = 11.558$ Å (each supercell contains two SnSe layers) and *Fm* $\bar{3}$ *m*-SnSe lattice parameters of $a = b = c = 4.247$ Å. These results agree well with experimental data (*Pnma*-SnSe: $a = 4.15$ Å, $b = 4.45$ Å, and $c = 11.50$ Å; *Fm* $\bar{3}$ *m*-SnSe: $a = b = c = 4.24$ Å)^{44,45}. From the atomic structures, one observes that when the even and odd numbered layers in *Pnma*-SnSe alternatively translate along the $\pm y$ -direction by $0.18 \times b$ (green arrows in Fig. 1a), this phase can change into *Fm* $\bar{3}$ *m*-SnSe. During this internal coordinate shuffling, the supercell transformation strain is actually small (compared with, e.g., ref. ⁴⁶); thus, little mesoscopic elastic constraint strain energy is required when a certain embedded region undergoes transformation. The volume difference between the two phases is within 0.5%. These facts demonstrate that the phase transition is martensitic and displacive, without requiring random atomic diffusion. Hence, the time scale of the phase transition can be greatly reduced, and the energy input to drive the phase transition is also small.

Our DFT calculations show that *Pnma*-SnSe has a lower ground state energy than *Fm* $\bar{3}$ *m*-SnSe by 17 meV per formula unit (meV/f.u.). This agrees well with previous DFT works⁴³. To estimate the energy barrier between the two phases and phase transition kinetics, we apply the cell-variable nudged elastic band (NEB) method^{47,48} to calculate the reaction path versus total energy. As shown in Fig. 2a, the energy barrier from *Pnma*-SnSe to *Fm* $\bar{3}$ *m*-SnSe is calculated to be 42 meV/f.u., corresponding to 123 J/cm³. This value is much smaller than the energy barrier from monolayer 2H-MoTe₂ to 1T'-MoTe₂ (~ 2000 J/cm³). The phonon spectrum of the saddle point crystal structure is shown in Fig. 2b, where only one large imaginary optical branch can be observed (at Γ). This imaginary mode corresponds to reaction coordinate shuffling to the *Pnma* phase, while the imaginary modes at Z (0, 0, 1/2) correspond to the transition to *Fm* $\bar{3}$ *m*. When the system transits back from *Fm* $\bar{3}$ *m*-SnSe to *Pnma*-SnSe, the energy barrier will be 25 meV/f.u. (73 J/cm³). By applying the Arrhenius law to estimate the transition rate, $k = \nu_0 \exp\left(-\frac{NE_b}{k_B T}\right)$ (where E_b is the energy barrier, N is the total number of formula units, and $\nu_0 = 10^{-12}$ s is the trial frequency), we note that *Fm* $\bar{3}$ *m*-SnSe can exist for over 20 years at room temperature ($T = 300$ K) when $N = 60$ (~ 3 nm³). On the other hand, the moderate energy barrier value *per unit* also indicate that the phase change between the two phases may be triggered by intermediate external field energy input with fast kinetics.

One fascinating feature during this structural phase transformation is the accompanying topological





electronic phase transition. As previously discussed, *Pnma*-SnSe is a topologically trivial semiconductor, with its highest valence and lowest conduction band located far from the Fermi level [Fig. 3a, left panel]. In contrast, the topologically nontrivial band gap insulator *Fm3m*-SnSe has a valence and conduction band inversion at the L-point in the Brillouin zone [Fig. 3b, left panel]. We plot the calculated band dispersions in the Supplementary Information, Fig. S2. Such a band topology change leads to quite a few important contrasting properties between the two phases, such as robust metallic surface states without backscattering. During a topological phase transition, a band gap closing and reopening process usually occurs. Thus, we also calculated the band gap value variation along the reaction path [Fig. 2a]. The band gap closing structure lies in the *Fm3m*-SnSe energy basin. Here, we show that the optical responses to an LPL of the two phases are very different. One can examine the

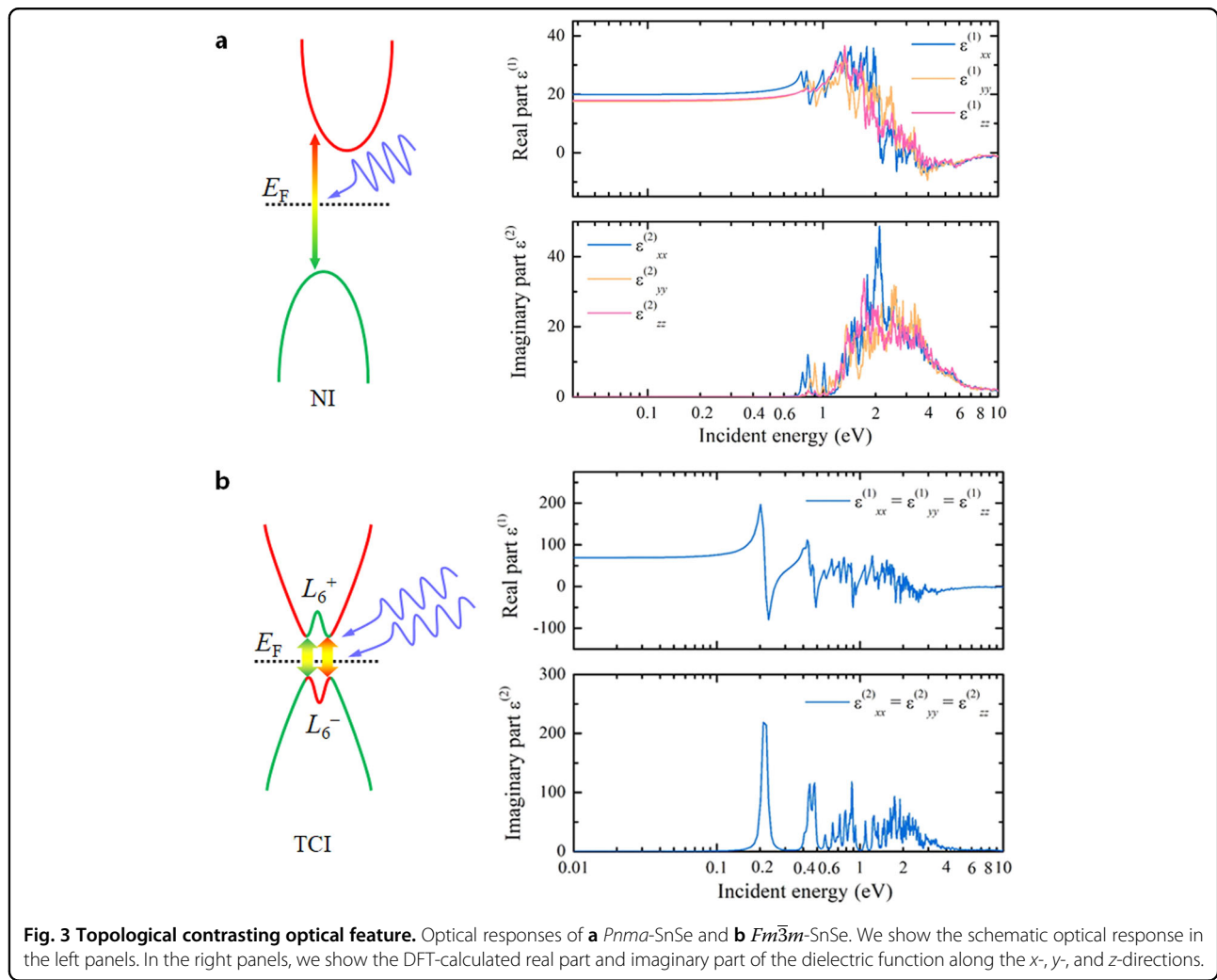
electron-contributed dielectric function based on the random phase approximation (RPA)^{49,50} via

$$\epsilon(\omega) = 1 - \frac{e^2}{(2\pi)^3 \epsilon_0} \int d^3\mathbf{k} \sum_{c,v} \frac{\langle u_{v,\mathbf{k}} | \nabla_{\mathbf{k}} | u_{c,\mathbf{k}} \rangle \langle u_{c,\mathbf{k}} | \nabla_{\mathbf{k}} | u_{v,\mathbf{k}} \rangle}{E_{c,\mathbf{k}} - E_{v,\mathbf{k}} - \hbar\omega - i\xi}. \quad (2)$$

Here, $|u_{n,\mathbf{k}}\rangle$ and $E_{n,\mathbf{k}}$ are the periodic part of the Bloch wavefunction and its corresponding eigenvalue of band n at \mathbf{k} , with indices v and c representing valence and conduction bands, respectively. ξ is a phenomenological damping parameter representing the temperature and disorder effects of the sample. From the above equation, one sees that the real part of the dielectric function is determined by two factors: (i) the direct energy band gap ($E_{c,\mathbf{k}} - E_{v,\mathbf{k}}$) and (ii) the Berry connection $\tilde{A}_{nm}(\mathbf{k}) = i\langle u_{n,\mathbf{k}} | \nabla_{\mathbf{k}} | u_{m,\mathbf{k}} \rangle$. Hence, compared with the NI *Pnma*-SnSe, the TCI *Fm3m*-SnSe has not only a relatively small band gap but also a larger Berry connection magnitude owing to its inverted band order with an enhanced band correlation. These facts indicate that the magnitude of $\epsilon^{(1)}$ of *Fm3m*-SnSe should be much larger than that of *Pnma*-SnSe, giving a large contrast of their NBE optical responses.

We thus calculate the dielectric functions of the two phases by choosing $\xi = 0.025$ eV, as shown in the right panels of Fig. 3a (*Pnma*-SnSe) and Fig. 3b (*Fm3m*-SnSe). Due to the geometric anisotropy, the x -, y -, and z -components of $\epsilon(\omega)$ of *Pnma*-SnSe are slightly different. In our current setup, when the incident photon energy is less than the direct band gap ($\hbar\omega < 0.70$ eV, where $\epsilon^{(2)}(\omega)$ is zero), the real parts of the dielectric functions of *Pnma*-SnSe almost remain constant, with $\epsilon_{xx}^{(1)}(\omega) = 19.9$, $\epsilon_{yy}^{(1)}(\omega) = 17.5$, and $\epsilon_{zz}^{(1)}(\omega) = 17.9$. On the other hand, the real parts of the dielectric functions of isotropic *Fm3m*-SnSe below the direct band gap are much larger. For example, at an incident energy $\hbar\omega_0 = 0.17$ eV, the calculated values are $\epsilon_{xx}^{(1)}(\omega_0) = \epsilon_{yy}^{(1)}(\omega_0) = \epsilon_{zz}^{(1)}(\omega_0) = 109.9$, which are nearly six times those of *Pnma*-SnSe at the same incident photon energy. We also plot the optical response of the DFT-calculated saddle point in the Supplementary Information (Fig. S3). We use a simplified $\mathbf{k}\cdot\mathbf{p}$ model to illustrate the topological contribution to the optical responses of *Fm3m*-SnSe (see the Supplementary Information for details). We find a relationship between the band gap at L-point (1/2, 1/2, 1/2) (measured as $2|m|$ in the model) and the dielectric constant, $\epsilon^{(1)}(0) = 1 + \alpha|m|^{-\gamma}$. For the topologically nontrivial band structure, the fitting coefficient α is much larger than that of the trivial band structure, indicating a large Berry connection contribution, as previously discussed.

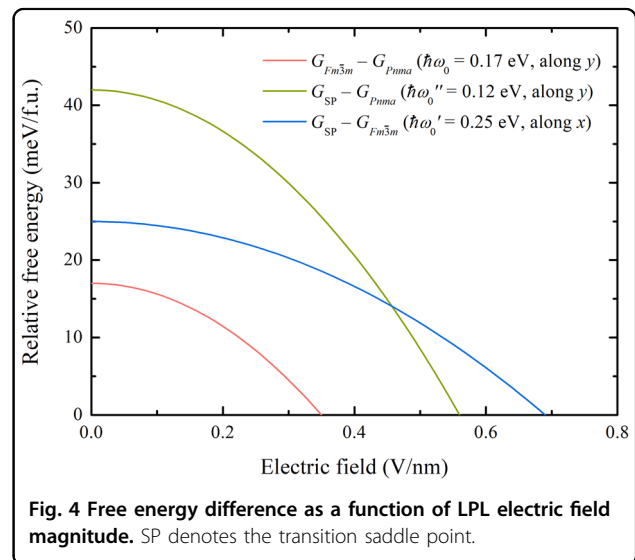
Owing to the centrosymmetric geometric feature of both phases, one can hardly apply a static electric field to drive the phase transition, as in ferroelectrics.



Alternatively, here, we propose a noncontacting optomechanical approach. According to our previous discussions, the free energies G_E (Eq. 1) under LPL pulse ($\hbar\omega_0 = 0.17$ eV) exposure of the two phases are different. Taking a *y*-directional LPL as an example (the other directions are similar), we calculate the free energy difference between the two phases under different electric field magnitudes (Fig. 4),

$$\Delta G(\mathcal{E}_0^y) = [E^{Fm\bar{3}m} - E^{Pnma}] - \frac{1}{2}\Omega\epsilon_0 [\epsilon_{yy}^{(1),Fm\bar{3}m}(\omega_0) - \epsilon_{yy}^{(1),Pnma}(\omega_0)] (\mathcal{E}_0^y)^2. \quad (3)$$

Here, Ω is the volume of a formula unit, and ϵ_0 is the vacuum permittivity. As the electric field magnitude ϵ_0 increases, the Gibbs free energy difference ΔG quadratically reduces to zero. We see that the critical electric field is 0.35 V/nm. Above this value, LPL exposure makes



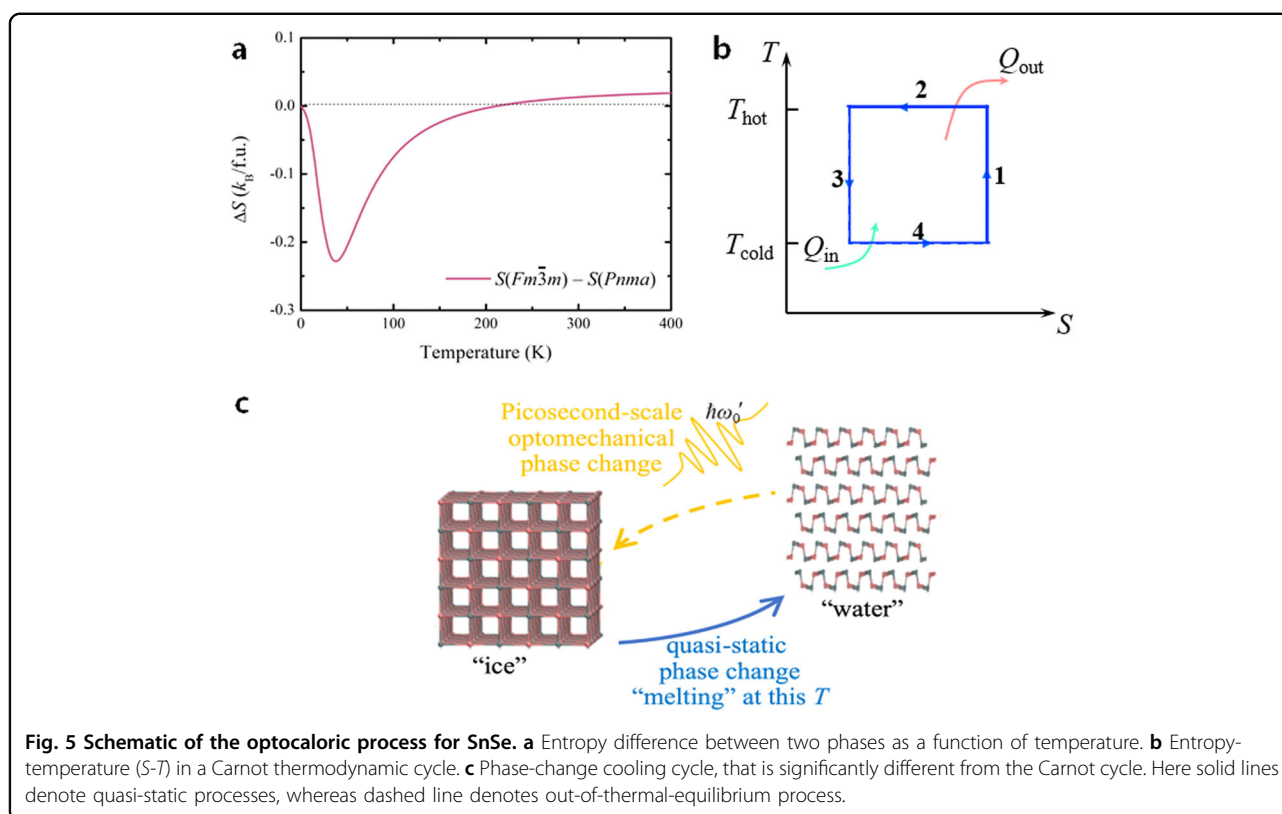
Fm $\bar{3}$ *m*-SnSe more stable, enabling a martensitic topological phase transition. To drive the opposite phase transition (from *Fm* $\bar{3}$ *m*-SnSe to *Pnma*-SnSe), even though the *Pnma* phase has a lower energy, we can apply a laser frequency at $\hbar\omega_0' = 0.25$ eV to accelerate the process. At this incident energy, the calculated $\epsilon_{xx}^{(1)}(\omega_0')$ values are 20.1, 41.2, and 6.5 for *Pnma*-SnSe, the transition saddle point, and *Fm* $\bar{3}$ *m*-SnSe, respectively. We estimate the electric field required to drive an ultrafast barrier-free phase transformation. For the *Pnma* to *Fm* $\bar{3}$ *m* transition, the incident LPL pulse can be $\hbar\omega_0'' = 0.12$ eV along the *y*-direction, and the calculated dielectric functions are $\epsilon_{yy}^{(1)}(\omega_0'') = 17.2$, 107.5 and 78.7 for *Pnma*, the saddle point and *Fm* $\bar{3}$ *m*, respectively. Hence, the electric field strength of 0.56 V/nm would drive a barrier-free phase transformation. For the *Fm* $\bar{3}$ *m* to *Pnma* transition, an electric field along the *x*-direction of 0.69 V/nm (incident energy $\hbar\omega_0' = 0.25$ eV) can suppress the energy barrier. When the bulk energy barrier (in units of meV/f.u.) vanishes, the transition kinetics is similar to that of spinodal decomposition, but in terms of the phonon displacement⁴⁸ instead of the chemical composition order parameter. With such a driving force that causes a vanishing bulk energy barrier, the typical nucleation-growth kinetics can be avoided, and the transition process could occur within picoseconds. We also illustrate this process (see the Supplementary Information for details), which reveals that the barrier-free phase transition occurs with a discontinuity of the electric displacement. Note that the phase transition is not temperature driven. Therefore, it does not require a large amount of latent heat to trigger the phase transition, as in the conventional temperature-driven process.

Since standard DFT calculations underestimate the band gap, here, we also use a more accurate approach to verify our calculations. As shown in Fig. S4 (Supplementary Information), we plot the real parts of the dielectric functions of both phases, calculated by the hybrid functional HSE06^{51,52}, which has been proven to correct the band gap underestimation of the GGA approach. We find that the overall trends are the same. If the incident photon energy is chosen to be $\hbar\omega_0 = 0.34$ eV, then the calculated values for *Pnma*-SnSe are $\epsilon_{xx}^{(1)}(\omega_0) = 14.0$, $\epsilon_{yy}^{(1)}(\omega_0) = 12.4$, and $\epsilon_{zz}^{(1)}(\omega_0) = 12.8$ and for *Fm* $\bar{3}$ *m*-SnSe are $\epsilon_{xx}^{(1)}(\omega_0) = \epsilon_{yy}^{(1)}(\omega_0) = \epsilon_{zz}^{(1)}(\omega_0) = 70.7$. Quasi-particle calculations with exciton binding correction (GW-BSE)^{53–56} are also performed (Fig. S5). The dielectric function difference between the two phases is much larger. At an incident energy of $\hbar\omega_0 = 0.14$ eV, the calculated results are $\epsilon_{xx}^{(1)}(\omega_0) = \epsilon_{yy}^{(1)}(\omega_0) = \epsilon_{zz}^{(1)}(\omega_0) = 185.0$ (*Fm* $\bar{3}$ *m*) and $\epsilon_{xx}^{(1)}(\omega_0) = 10.2$, $\epsilon_{yy}^{(1)}(\omega_0) = 8.5$, and $\epsilon_{zz}^{(1)}(\omega_0) = 11.7$ (*Pnma*). The corresponding electric field strength to trigger the phase transition from *Pnma* to *Fm* $\bar{3}$ *m* is 0.25 V/nm (laser power of 8.3×10^9 W/cm²). The

dielectric function value of the TCI *Fm* $\bar{3}$ *m*-SnSe is larger than that of *Pnma*-SnSe, indicating the robustness of the optomechanically driven martensitic phase transition. To accelerate the transition from *Fm* $\bar{3}$ *m* to *Pnma*, an incident light of $\hbar\omega_0' = 0.5$ eV (along *x*) can be applied, with its calculated $\epsilon_{xx}^{(1)}(\omega_0')$ being 12.3 and 1.8 for *Pnma* and *Fm* $\bar{3}$ *m*, respectively.

We then propose that this optomechanically driven phase transformation of SnSe will lead to a promising cooling mechanism⁵⁷, which we refer to as the optocaloric effect. We calculate the entropy ($S = S_{ph} + S_{el}$, where S_{ph} and S_{el} are the phononic and electronic entropies, respectively) difference between the two phases (Fig. 5a). The calculation details can be found in the Supplementary Information. The largest entropy change appears at $T = 40$ K, with $\Delta S = -0.23$ k_B /f.u. At room temperature ($T = 300$ K), *Fm* $\bar{3}$ *m*-SnSe has a higher entropy than *Pnma*-SnSe by 0.01 k_B /f.u. (k_B is the Boltzmann constant, corresponding to 0.5 J K⁻¹ kg⁻¹). Such latent heat ($T\Delta S$) between two phases (one stable, one metastable, at T when optical field is turned off) can be used to drive cooling, similar to producing ice from liquid water in a summer day using a specially made mechanical shocking device, and then letting ice \rightarrow liquid water for cooling purposes on that summer day. This is not a Carnot cycle (Fig. 5b), which is based on a single-phase medium (ideal gas) and consisting of four quasi-static thermodynamic legs (two isothermal which contributes sensible heat, and two adiabatic legs, and all four legs require gradual pressure/volume changes). Here, instead, we propose to use latent heat rather than sensible heat during a two-legged cycle (Fig. 5c): in one leg of the loop we use optomechanical shock to non-quasistatically drive the phase transition from the stable \rightarrow metastable phase (stable and metastable phases defined when the optical field is turned off, for that T), and in the other leg we allow the metastable phase to relax back to the stable phase thermally. This will be a two-step loop. During the first step, the *Fm* $\bar{3}$ *m*-SnSe phase absorbs latent heat (Q_{in}) and quasi-statically (and isothermally) transforms to *Pnma*-SnSe, like ice melting in a cold drink. In the second step, we apply a laser pulse to drive *Pnma*-SnSe back to the *Fm* $\bar{3}$ *m*-SnSe phase. This leg is not a quasi-static process (out of local thermal equilibrium, since the reaction coordinate gains a lot more kinetic energy than the other vibrational degrees of freedom), which cannot be represented by a thermodynamic state curve in an equilibrium thermodynamic macro-state plot like Fig. 5b.

We also perform calculations for other analogous group-IV monochalcogenide compounds (Fig. S7). During geometric optimization, *Pnma*-PbSe and *Pnma*-PbTe relax to the *Fm* $\bar{3}$ *m* structure owing to the large size of the Pb ion. *Fm* $\bar{3}$ *m*-PbS is also energetically more stable than *Pnma*-PbS. Hence, alloyed materials, such as $Pb_{1-x}Sn_xX$



($X = \text{S, Se, Te}$)⁵⁸ compounds, are possible candidates for tuning $Pnma \leftrightarrow Fm\bar{3}m$ transitions. For example, when $x = 0.30$, experimental evidence shows that the topological transition temperature is ~ 250 K in $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ ⁵⁹. We also know that in the $Fm\bar{3}m$ -GeTe and $Fm\bar{3}m$ -SnTe compounds, there is a spontaneous cubic-to-rhombohedral structural phase transition in which the sublattice Ge/Sn and Te atoms displace along the $[111]$ direction^{60,61}. This forms a ferroelectric state, which is topologically trivial with a wide band gap. Under hydrostatic pressure, the rocksalt $Fm\bar{3}m$ phase can be dynamically stable. Hence, unless under pressure, the phase transition between the two phases is not accompanied by topological changes in the electronic band structure, but nonetheless has certain dielectric response contrast. The GeSe, GeS, SnS, and PbS compounds all have similar results to SnSe, whose $Pnma$ and $Fm\bar{3}m$ phases are locally stable when not optically pumped. The optical responses of these compounds are also similar to those of SnSe (Fig. S8).

Conclusion

In conclusion, we systematically calculate the energetics and optical responses of the SnSe compound and chemical analogues in their low temperature phases, namely, normal insulator $Pnma$ and topological crystalline insulator $Fm\bar{3}m$. We propose that the phase transition can

also be driven when one applies a pulsed laser with a selected frequency. Such a topological phase transition, similar to the transformation of TMD monolayers from 2H to 1T' but with lower energy barrier and energy input, belongs to martensitic displacive phase transitions, but with very little transformation strain during and after the transformation, and thus has low elastic constraint penalty energy, ensuring fast kinetics and reversibility. We predict a promising optocaloric effect in SnSe based on the phase-change cycle, taking advantage of the low dissipation and stress of such rapid optically driven transitions, which could be useful as a refrigerant.

Acknowledgements

J.Z. acknowledges the National Natural Science Foundation of China under Grants Nos. 21903063 and 11974270, and the Young Talent Startup Program of Xi'an Jiaotong University. S.Z. acknowledges the NSFC grant under No. 11904350. J.Z. thanks Xiaoyin Li for helpful discussions on phonon simulations.

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Conflict of interest

The authors declare that they have no conflict of interest.

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Supplementary information is available for this paper at <https://doi.org/10.1038/s41427-019-0188-9>.

Received: 26 April 2019 Revised: 28 August 2019 Accepted: 30 October 2019

Published online: 10 January 2020

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