Pressure-induced topological phase transitions in rocksalt chalcogenides

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By means of a comprehensive theoretical investigation, we show that external pressure can induce topological phase transitions in IV–VI semiconducting chalcogenides with a rocksalt structure. These materials satisfy mirror symmetries that are needed to sustain topologically protected surface states, at variance with time-reversal symmetry that is responsible for gapless edge states in $\mathcal{Z}_2$ topological insulators. The band inversions at high-symmetry points in the Brillouin zone that are related by mirror symmetry are brought about by an "asymmetric" hybridization between cation and anion sp orbitals. By working out the microscopic conditions to be fulfilled in order to maximize this hybridization, we identify materials in the rocksalt chalcogenide class that are prone to undergo a topological phase transition induced by pressure and/or alloying. Our model analysis is fully confirmed by complementary advanced *first-principles* calculations and *ab initio*-based tight-binding simulations.

I. INTRODUCTION

Semiconducting IV–VI chalcogenides CA ($C =$ Ge, Sn, Pb and $A =$ S, Se, Te) represent an attractive class of materials, due to their unique structural and electronic properties. The most interesting compounds—SnTe, GeTe, and the lead chalcogenides PbA—display a rocksalt structure.[1] Both SnTe and GeTe have been long known for their ferroelectric properties in the low-temperature distorted structure,[2] whereas PbA possess potential relevance for thermoelectric and optoelectronic applications[3]. Their outstanding properties have been characterized by a variety of experimental techniques.[3,4] In parallel, a large number of theoretical investigations, carried out with different methods ranging from tight-binding (TB) to density-functional theory (DFT) calculations, have addressed their peculiar electronic structure.[5–10] Interest in this material class has been renewed because of relativistic effects that are relevant for future spintronic devices. For example, a giant Rashba effect has been predicted in the ferroelectric phase of bulk GeTe,[11] while SnTe is a topological crystalline insulator (TCI) with spin-polarized surface states.[12,13] These observations motivated us to investigate the possibility of topological phase transitions in this class of narrow-gap semiconductors.

In the $\mathcal{Z}_2$ class of topological insulators (TIs), time-reversal symmetry ensures topologically protected edge states.[14,15] An odd number of Dirac cones pinned at time-reversal-invariant momenta (TRIM), as found, e.g., in Bi$_{1-x}$Sb$_x$ and Bi$_2$Se$_3$,[14,15] distinguishes a $\mathcal{Z}_2$ TI from a conventional band insulator. In contrast, crystal symmetries play a central role in the class of TCIs.[16,17] Beside symmetry requirements, band inversions in the bulk insulating electronic structure and strong spin-orbit coupling (SOC) are needed for metallic surface states to appear. In face-centered-cubic (fcc) TCIs, a mirror symmetry causes the appearance of an even number of Dirac cones on surfaces preserving the symmetry [see Figs. 1(a) and 1(b)]. These cones are situated off the TRIM $\bar{X}$ within the $\bar{\Gamma}$-$\bar{X}$ line of the surface Brillouin zone.[12] Since all members of the cubic IV–VI class share the same crystal symmetries, all of them and their alloys may be prone to topological phase transitions. Such transitions, characterized by a nonzero mirror Chern number,[12,18] have been proposed for PbTe and

PbSe under pressure,[10,12] and were experimentally observed in ternary alloys Pb$_{1-x}$Sn$_x$(Se,Te) as a function of doping.[19–22] These findings are not simply explained by the SOC strength: Although SOC in Pb ($Z = 82$) is larger than in Sn ($Z = 50$), PbTe is nonetheless a conventional band insulator, as opposed to the TCI SnTe. This clearly calls for a deeper understanding of the microscopic origin of the band inversions.

In this paper we show that in principle all members of the rocksalt chalcogenide class can be turned into TCIs under pressure, with the only exception of GeTe. The methods used comprise advanced *first-principles* simulations and *ab initio*-based TB calculations. Consistent with sophisticated GW computations,[10] we find that the fundamental gap of lead chalcogenides shrinks upon applying external pressure, closes at a critical pressure, and subsequently reopens with an inverted band character. This behavior is typical of a topological phase transition and is exemplified for PbTe in Fig. 2, where a relativistic TB scheme[6] for the semi-infinite system was used.[23,24] As long as the fcc structure is preserved, these band inversions cause metallic surface states [Fig. 2(c)].

To benchmark the reliability of our predictions, we performed accurate DFT calculations with hybrid functionals,[25] as implemented in VASP.[26–28] These improve significantly with respect to local-density or generalized-gradient approximations, especially for narrow-gap semiconductors.[9,29] For PbTe, we find the fundamental band gap at L to close at a volume ratio of $V/V_0 = 0.91$ [V_0 is the equilibrium volume; see also Fig. 2(b)] that is accompanied by band inversion (Fig. 3). This finding corroborates the topological phase transition deduced from TB calculations (cf. Fig. 2). At variance with PbTe, hole pockets appear in the electronic structure of GeTe, concomitantly with the pressure-induced closure of the fundamental gap, thus triggering a semimetallic state instead of a TCI. These essential differences require clarification in a microscopic picture.

II. SEMI-EMPIRICAL DISCUSSION

Many peculiar electronic properties of PbA were resolved by noting that the Pb-6s band lies below the top of the valence band. The existence of an occupied cation-s band
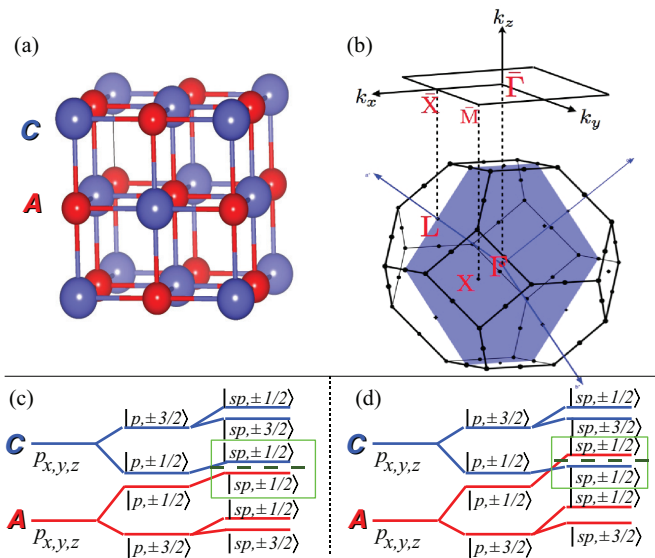
FIG. 1. (Color online) (a) Crystal structure and (b) Brillouin zone of rocksalt chalcogenides, showing one mirror plane (green) containing the high-symmetry points Γ, L, and X as well as their projection onto the [001] surface. Schematic representation of the band structure at the L point in the topologically trivial phase (c) and upon pressure-induced enhancement of sp hybridization (d). Dashed lines separate occupied from unoccupied energy levels.

leads to strong level repulsion at L, explaining the narrow band gap E_g and its unusual ordering within the series.[8,9] The central role of s electrons can be deduced within the framework of linear combinations of atomic orbitals.[30] The only nonzero matrix elements at L in the nearest-neighbor approximation are those describing the hybridization between cation (anion) s and anion (cation) p states. Because of SOC, this hybridization close to the Fermi energy involves mainly a combination of atomiclike p states on C and A sites, with a total angular momentum $j = 1/2$, namely, $|\pm 1/2\rangle = (|p_x, \mp 1/2\rangle \pm i |p_y, \mp 1/2\rangle + |p_z, \pm 1/2\rangle)/\sqrt{3}$, and energies $\bar{\epsilon}_{p,A(C)} = \epsilon_{p,A(C)} \pm 2\lambda_{A(C)}$; here, $\epsilon_{p,A(C)}$ and $\lambda_{A(C)}$ are the orbital energy and the SOC constant of the C (A) ion, respectively. In the atomic limit, corresponding to the topologically trivial phase, $\Delta_0 \equiv \bar{\epsilon}_{p,C} - \bar{\epsilon}_{p,A} > 0$ means occupied A and unoccupied C p shells [Fig. 1(c)]. The hybridization with the s states pushes both C and A p levels to higher energies; this energy shift is roughly proportional to the squared effective hopping interaction t_{sp} and inversely proportional to the energy differences $\Delta_1 \equiv \bar{\epsilon}_{p,C} - \epsilon_{s,A}$ and $\Delta_2 \equiv \bar{\epsilon}_{p,A} - \epsilon_{s,C}$. The energy gap at L can then be approximated as $E_g \approx \Delta_0 + 10 t_{sp}^2 (\Delta_1^{-1} - \Delta_2^{-1})/3$. Hence, for band inversion to occur, two conditions have to be satisfied: (1) The energy separation Δ_0 between p states must be sufficiently small, and (2) the sp hybridization should be strongly "asymmetric." This asymmetry is realized if $\Delta_1 \gg \Delta_2$, i.e., if the cation (anion) s level is energetically close to (far from) the anion (cation) p states.

The band gap is directly related to the $\vec{k} \cdot \vec{p}$ Hamiltonian at L, $\hat{H} = m\sigma_z$;[5,12] $\sigma_z = \pm 1$ corresponds to the p character on C and A sites, respectively. A negative $m \equiv E_g/2$ implies that conduction and valence bands at L derive respectively from A
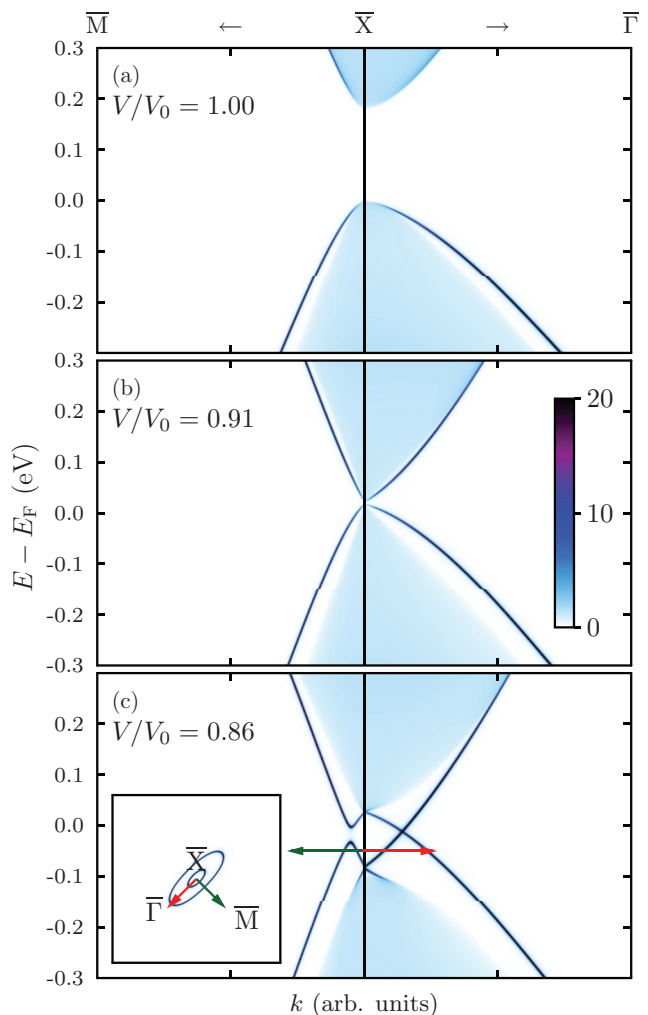

FIG. 2. (Color online) Topological phase transition in PbTe upon pressure, calculated by a TB method. For selected volume ratios V/V_0, the spectral density of the topmost layer of the (001) surface is represented in a color scale [(b), in states $/eV$]. Topological trivial phases with mirror Chern number 0 appear for the equilibrium volume (a) and close to the critical pressure (b). A topological nontrivial phase (c) shows a mirror Chern number of -2. Its Dirac surface state is depicted in a constant-energy cut around $\overline{X}$ at E_F -0.05 eV [inset in (c)]. A k path shown also in (c) is marked by arrowed lines. The k axis common to (a)–(c) shows 2/5 of the $\overline{M}$-$\overline{X}$ and $\overline{X}$-$\overline{\Gamma}$ lines around $\overline{X}$ [cf. Fig. 1(b)].

and C ions. A reversal of m in the presence of the fcc-structure mirror symmetries implies a topological phase transition with an associated change of the mirror Chern number.[12] A large SOC is required to fulfill the first condition. The second condition, on the other hand, could in principle be controlled by alloying ternary solid solutions $C_x C'_{1-x} A$ (along the path pursued in Refs. [19–22]) or $CA_x A'_{1-x}$.[31] Because the band inversion is proportional to the strength of the sp hybridization, $t_{sp} \propto d^{-2}$, a straightforward way to induce a topological phase transition is to apply external pressure.[10,12,30]

Guided by these considerations, we performed an empirical screening within the rocksalt chalcogenide class, using different TB and *ab initio*-based TB parametrizations[6,30,32] (Table I). Trends are consistent and allow to loosely identify three

TABLE I. Estimated relevant quantities from Harrison's (Ref. 30) and Lent's (Ref. 6, in brackets) parametrizations. Values in square brackets were obtained from first principles by projecting DFT bands on a TB model using maximally localized Wannier-functions (Ref. 32). SOC and lattice constants a_0 are taken from Refs. 33 and 1, respectively.

	PbTe	SnTe	PbS	PbSe	GeTe
Δ_0 (eV)	0.71	1.35	3.15	2.09	1.19
	(1.72)	(0.95)	(3.92)	(3.29)	(0.28)
	[2.68]	[1.8]	[4.72]	[4.00]	[1.64]
Δ_1 (eV)	10.08	10.71	13.77	13.29	10.55
	(12.70)	(13.13)	(16.25)	(15.75)	(11.92)
	[12.16]	[11.31]	[15.21]	[15.10]	[10.29]
Δ_2 (eV)	4.32	4.75	1.89	2.95	6.63
	(7.16)	(6.69)	(5.59)	(5.18)	(8.51)
	[5.80]	[5.44]	[4.37]	[4.84]	[5.68]
a_0 (Å)	6.462	6.327	5.936	6.124	6.009

subclasses: (i) The first subclass, comprising PbTe and SnTe, is characterized by a relatively small Δ_0 (mainly due to the large λ_{Te}) and similar differences $\Delta_1^{-1} - \Delta_2^{-1}$. In this respect, the main reason why SnTe is a TCI but PbTe is not could be the smaller equilibrium volume of the former with respect to the latter. In turn, a relatively small pressure could tune the topological transition in PbTe,[12] and the doping-dependent topological transition in Pb$_{1-x}$Sn$_x$Te could be ascribed to a (chemical) pressure effect. (ii) The second subclass comprises PbS and PbSe and shows Δ_0's approximatively twice as large as those of the first subclass, due to smaller λ_A. However, Δ_2 is much smaller than Δ_1; it is thus very likely that a reduction of the lattice constant and the associated increase of t_{sp} could result in band inversion (due to the strongly asymmetric sp hybridization) and, hence, in a topological phase transition. (iii) GeTe, belonging to the third class, even though displaying
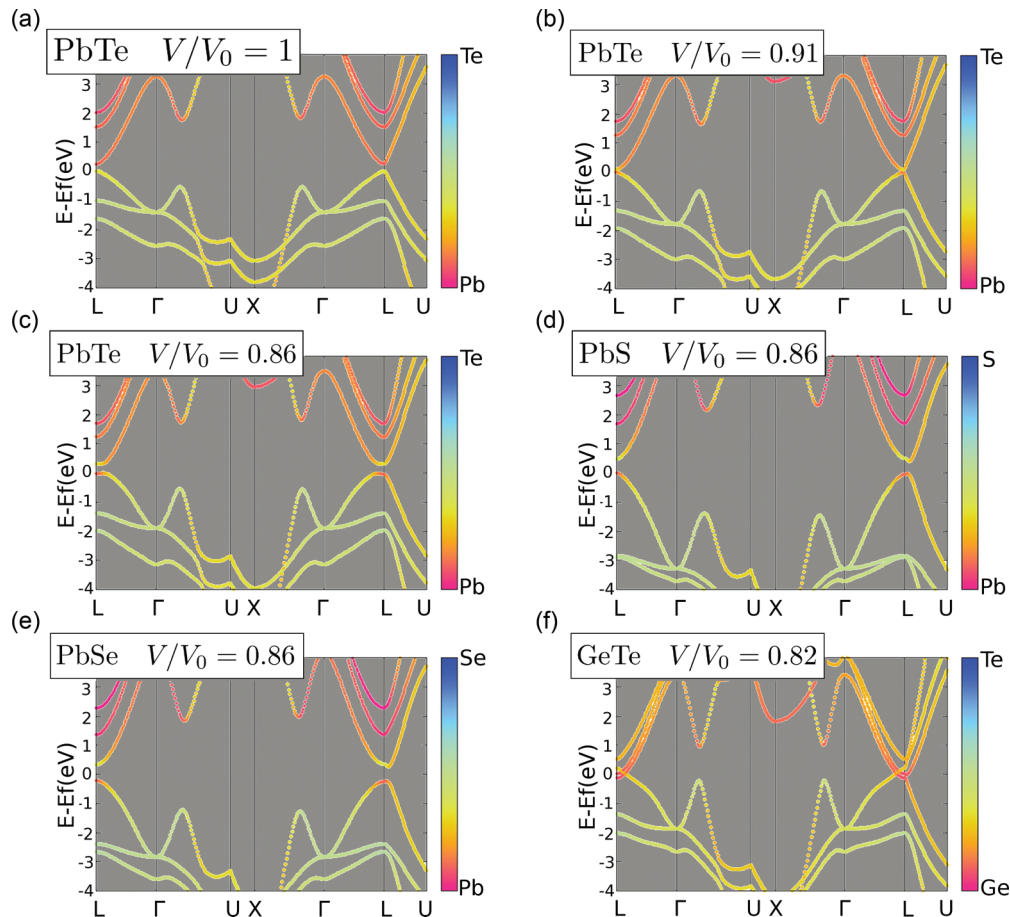

FIG. 3. (Color online) DFT electronic structures of selected rocksalt chalcogenides for different volume ratios V/V_0, with band characters highlighted by a color scale (anions: blue; cations: red).

a small Δ_0, does not seem to fulfill condition (2) above. Thus, a reopening of the gap is unlikely and a transition to a metallic state is expected upon applying pressure (Fig. 3).

III. RESULTS

Our DFT calculations confirm this scenario. The band inversion is highlighted for PbA at selected volumes (Fig. 3). For PbTe, the closure of the band gap shows up at a critical volume of $0.92V_0$; hence, the band inversion has already occurred at a volume ratio $V/V_0 = 0.91$ (pressure ~ 4 GPa), with a predominant Te character in the conduction band at L. The negative gap increases upon further decreasing the volume ($V/V_0 = 0.86$ in Fig. 3). Indeed, the atomic and orbital resolved character of the valence (conduction) band at L shows a predominant Pb-s and Te-p (Pb-p and Te-s) contribution at V_0, whereas an opposite character appears below the critical volume.[34] The same trend with pressure holds for both PbS and PbSe, with critical volumes of about $0.94V_0$ and $0.96V_0$ (TB: $0.91V_0$ and $0.96V_0$; pressure 4.2–6.3 and ~ 2.4 GPa), respectively. The predicted critical pressures can be compared with those at which PbA undergo structural transitions, hence losing the fcc-structure symmetry required for the TCI transition; these are 2.98 GPa,[35] 6.01 GPa,[36] and 6.05 GPa (Ref. 37) for $A =$ S, Se, Te, respectively. Hence, in principle, the topological transition may be observed in high-pressure experiments on PbSe and PbTe, for which structural transitions happen at higher pressures than the predicted critical ones. For GeTe, on the other hand, the gap closes at a critical volume of $0.9V_0$ (pressure ~ 5 GPa). This finding is consistent with the smaller hybridization asymmetry. Furthermore, since the $j = 1/2$ and $j = 3/2$ manifolds in the conduction bands are close in energy due to small λ_{Ge}, a further increase of pressure pushes them both below the anion p states, thus turning GeTe into a semimetal (Table I and Fig. 3).

To provide further support for the pressure-induced topological phase transitions, we performed relativistic TB calculations for bulk PbTA and GeTe. The mirror Chern number is computed in the spirit of the spin Chern number.[38] Since the Bloch states are eigenstates of both the Hamiltonian and the mirror operator,[39] we separate them into two categories with mirror eigenvalues $\pm i$ and calculate the Berry curvature for both. The integral of the Berry curvature over the intersection of the mirror plane with the Brillouin zone yields Chern numbers $n_{\pm i}$, from which the mirror Chern number $c_{\text{m}} \equiv (n_{+i} - n_{-i})/2$ is obtained.[18] While GeTe is always topologically trivial, we find a mirror Chern number of -2 for band-inverted PbA. In summary, the numerical calculations corroborate the microscopic picture derived above.

IV. CONCLUSIONS

In conclusion, we have shown that a strongly asymmetric sp hybridization and a sizable SOC are necessary conditions for band inversions to occur at the L points and the related TCI state to arise in rocksalt chalcogenides. By performing a thorough analysis of pressure effects in the entire family of fcc chalcogenides, we verify the topological nature of the transition, as shown by nonzero mirror Chern numbers and gapless edge states at (001) surfaces. In principle, the predicted TCI transition may be experimentally investigated in PbTe and PbSe by using infrared or Raman spectroscopy, as recently proposed for pressure-induced transitions of $\mathcal{Z}_2$ topological order.[40,41] Furthermore, we suggest that topologically trivial lead chalcogenides could be turned into a topologically nontrivial state upon a combination of applied pressure and alloying *through anion substitution*, a yet unexplored path to engineer a TCI.[42] This scenario may be relevant for the experimental search of conducting edge states, as the carrier concentration, largely determined by the presence of cation or anion vacancies, can be easily controlled in lead chalcogenides during the crystal growth,[3] as opposed to SnTe, where a high concentration of cation vacancies is frequently found, resulting in an undesirable p-type degenerate conducting behavior.

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[29] For instance, LDA calculations predicted a negative pressure dependence of the lead chalcogenide band gap, which would suggest an inverted band structure at L. However, GW calculations have shown that this inversion is a spurious outcome of the local approximation for the exchange-correlation potential, which is known to place the conduction band too low in energy (that is, too small a band gap) (Ref. 10).

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[34] When projecting wave functions at L within muffin-tin spheres with radius = 1.73 Å and 1.54 Å for Pb and Te, respectively, the weights on Pb-s, Pb-p, Te-s, and Te-p are 0.24, 0.0, 0.0, and 0.36 for the valence band maximum (VBM), and 0.0, 0.36, 0.06, and 0.0 for the conduction band minimum (CBM) at the equilibrium volume for PbTe, whereas we find 0, 0.36, 0.06, and 0 for the VBM and 0.29, 0.0, 0.0, and 0.11 for the CBM at $V/V_0 = 0.86$.

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[42] For instance, in the PbSe$_x$Te$_{1-x}$ alloy, one expects an effect of chemical pressure [a_0(PbSe) $\ll a_0$(PbTe)] and of the band shifts. The latter "asymmetrize" the hopping interactions, so that for a doping of $x = 0.2$ one would get $\Delta_0 = 1$ eV, $\Delta_1 = 10.72$ eV, $\Delta_2 = 4.04$ eV, and $a_0 = 6.39$ Å in the VCA. Also on the basis of the smaller critical pressure predicted for PbSe with respect to PbTe, a topological transition is therefore likely to occur at reasonable values of applied pressure.