

Band inversion and the topological phase transition in (Pb,Sn)Se

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The recent discovery of a topological phase transition in IV-VI narrow-gap semiconductors has revitalized the decades-old interest in the bulk band inversion occurring in these materials. Here we systematically study the (001) surface states of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ mixed crystals by means of angle-resolved photoelectron spectroscopy in the parameter space $0 \leq x \leq 0.37$ and $300 \text{ K} \geq T \geq 9 \text{ K}$. Using the surface-state observations, we monitor directly the topological phase transition in this solid solution and gain valuable information on the evolution of the underlying fundamental band gap of the system. In contrast to common model expectations, the band-gap evolution appears to be nonlinear as a function of the studied parameters, resulting in the measuring of a discontinuous band-inversion process. This finding signifies that the anticipated gapless bulk state is in fact not a stable configuration and that the topological phase transition therefore exhibits features akin to a first-order transition.

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I. INTRODUCTION

Lead chalcogenides and related compounds have been studied intensely already throughout the last century [1,2]. These narrow-gap semiconductors are used for applications in infrared lasers [3] and detectors [4] as well as in thermoelectric devices [5,6]. They also exhibit a large range of peculiar fundamental properties, such as positive temperature and negative pressure coefficients of the energy gap [7] and nonparabolic band dispersions [8]. Moreover, for suitable compounds and parameter ranges, the band gap undergoes an inversion as a function of temperature, pressure [9], and composition [10,11]. Gapless states were predicted to form at the interface between inverted and noninverted insulating layers [12]. The interest in this class of materials was very recently renewed by the investigation of the so-called topological-crystalline-insulator (TCI) state in SnTe [13,14] as well as the solid solutions $(\text{Pb,Sn})\text{Te}$ [15] and $(\text{Pb,Sn})\text{Se}$ [16]. In this state of matter, the mirror symmetry present in the rocksalt structure ensures degenerate energy eigenvalues along mirror lines, and hence metallic surface states on certain high-symmetry surfaces [17], when the band gap is inverted. Additionally, these topologically protected surface states exhibit Dirac-like dispersions and they are spin momentum locked [15,18,19].

Although the tunable band inversion in the lead and tin chalcogenides has been established for decades, the details of the gap closing are still unknown. It is commonly expected (cf., e.g., most of the aforementioned references) that the size of the band gap goes to zero when a critical composition, temperature, or pressure is reached. Yet, a *completely closed*

band gap is naturally hard to observe experimentally. The lowest confirmed gap values are in the region of a few tens of millielectronvolts. For instance, in infrared absorption studies, the long-wavelength limit was not accessible [11] and very-low-energy laser emission seems to be hindered by plasmon-phonon excitations [9,20].

The recent discovery of the TCI phase and the appertaining surface states has opened a route to study the details of the band inversion in this class of materials by high-resolution photoelectron spectroscopy. The (001) surface states at the surface high-symmetry point \bar{X} lie within the bulk band gap just beyond the valence- and conduction-band edges projected from the bulk L points [13,16,18,21]. The same is true for the corresponding high-symmetry points of the (110) surface [17]. Hence, studying the surface-state evolution across a parameter range for which the band inversion occurs can give a reliable estimate of the band gap at L and thus further elucidate the process of the inversion.

In this Rapid Communication, we report on a systematic angle-resolved photoelectron spectroscopy (ARPES) study of (001)-oriented $(\text{Pb,Sn})\text{Se}$ mixed crystals. The topological phase boundary is established by an investigation of the evolution of the surface states around \bar{X} as a function of composition and temperature. Moreover, contrary to common theoretical expectations and conclusions from previous experimental work, our observations point to an unstable zero-gap state (ZGS) in the bulk material.

II. EXPERIMENTAL DETAILS AND RESULTS

The $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ ($0 \leq x \leq 0.37$) single crystals used in this study have been grown by the self-selecting vapor-growth method [22]. Their composition has been determined by means of x-ray diffraction as well as energy-dispersive x-ray spectroscopy. Powder x-ray diffraction confirmed the rocksalt structure [space group $Fm\bar{3}m$ (225)] both at room temperature and $T = 15 \text{ K}$. To avoid the necessity of extrinsic surface

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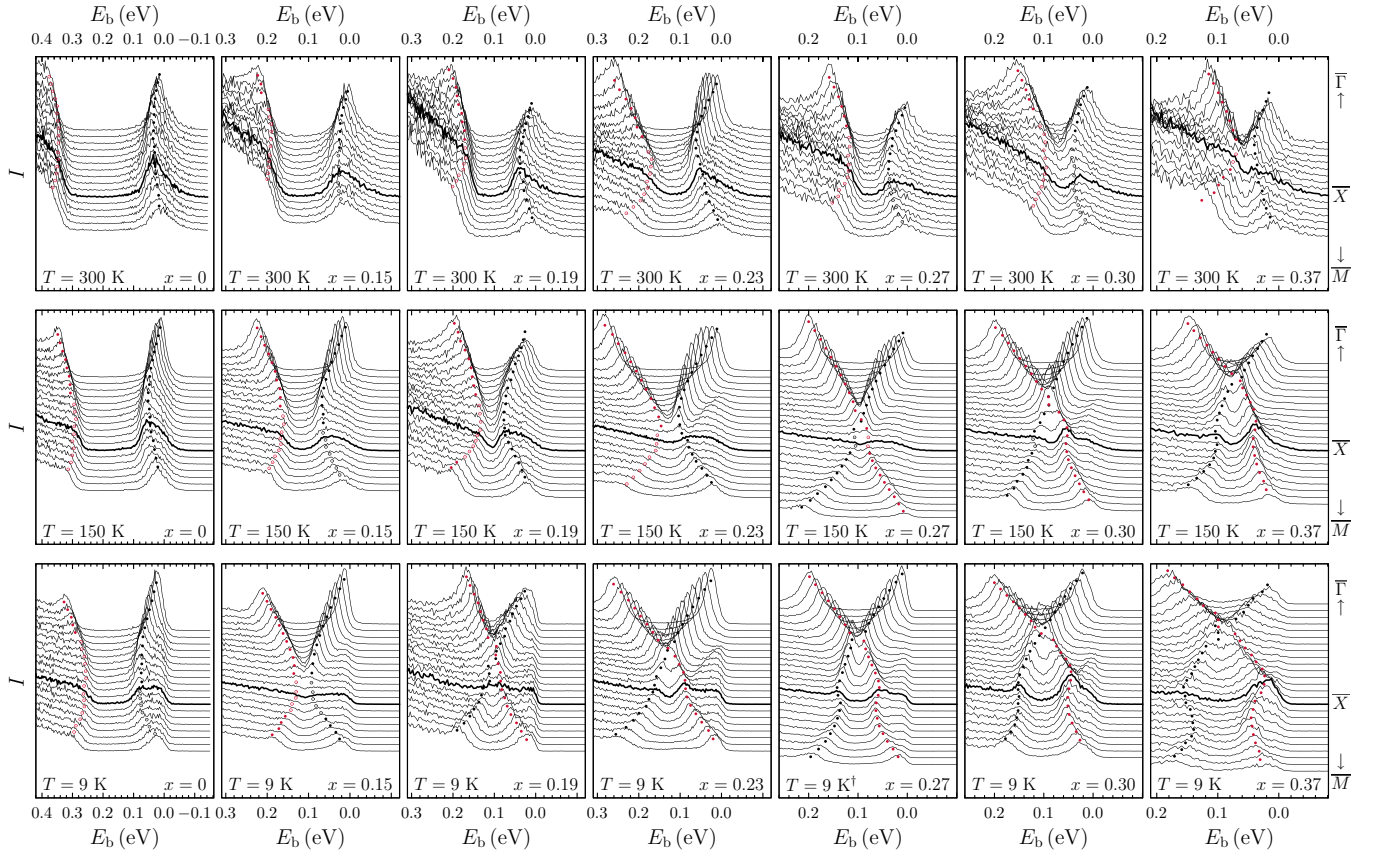


FIG. 1. (Color online) ARPES spectra in the vicinity of \bar{X} of the (001) surface of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ as a function of tin content x (varying with the columns) for three selected temperatures [25,26]. The observed surface states display a transition from an overall gapped state (low x or high T) [27] to a state that is gapless along the $\bar{\Gamma}$ - \bar{X} line (high x and low T) [28]. The energy-distribution-curve (EDC) intensity is shown on a linear scale and the spacing between neighboring EDCs is roughly given by $0.009\pi/a$, where $a(x, T)$ is the bulk lattice constant. In each panel, the solid circles mark the fitted Voigtian EDC peak positions; where no peaks are discernible, open circles mark the band edge. The latter positions are generally found to smoothly extrapolate the dispersion of the surface-state peak positions. The different colors are merely used to visualize the derived L_6^- and L_6^+ character of the valence- and conduction-band edges.

doping [23] which might alter the intrinsic electronic structure, bulk n -type crystals are used in this study. The ARPES measurements in the temperature range $300 \text{ K} \geq T \geq 9 \text{ K}$ have been conducted on samples cleaved along a (001) surface in ultrahigh vacuum. The experiments have been performed using the laser-based ARPES setup BALTAZAR equipped with a time-of-flight electron analyzer [24]. Linearly polarized light with a photon energy $h\nu = 10.5 \text{ eV}$ was used to excite the electrons. The total energy and crystal-momentum resolution was about 5 meV and better than 0.008 \AA^{-1} , respectively.

Characteristic ARPES spectra are shown in Fig. 1. The data in the vicinity of \bar{X} are plotted along the high-symmetry lines of the surface Brillouin zone ($\bar{\Gamma}$ - \bar{X} - \bar{M}). In all spectra surface states are discernible. While the samples at high temperature ($T = 300 \text{ K}$) exhibit gapped states for all x [27], at lower temperatures the spectra show a change from gapped surface states at low x to metallic (gapless) states crossing on the $\bar{\Gamma}$ - \bar{X} line at high x —the hallmark of the transition from a usual band insulator to a TCI [28]. A closer inspection of the spectra shows that for $x \leq 0.15$, the energy gap at \bar{X} ($\Delta_{\bar{X}}$) decreases when the temperature is lowered. The gap $\Delta_{\bar{X}}$ also shrinks with increasing x when the samples are kept at room temperature.

The opposite behavior is found for samples with high x at low temperatures.

As described above, the surface-state dispersion can be viewed as an envelope of the projected bulk bands. Hence, $\Delta_{\bar{X}}$ provides an estimate of the bulk band gap at L [13,16,18,21], and thus the observed qualitative trends are generally anticipated. They can be explained with the negative pressure coefficient of the energy gap (the lattice constant decreases with temperature as well as with increasing x) together with the phonon-related changes (cf. Ref. [1] and references therein). Also in line with the expectations is that for PbSe the top of the valence band changes more strongly than the bottom of the conduction band across the range of parameters—a direct consequence of the band repulsion due to the occupied Pb 6s level in the valence band [7,30].

III. ANALYSIS AND DISCUSSION

To gain more quantitative insight in the evolution of the energy gap, in particular, in the region where the gap is small, we plot the values of $\Delta_{\bar{X}}(x, T)$ in Fig. 2. The values shown represent the difference in the surface-state positions at the

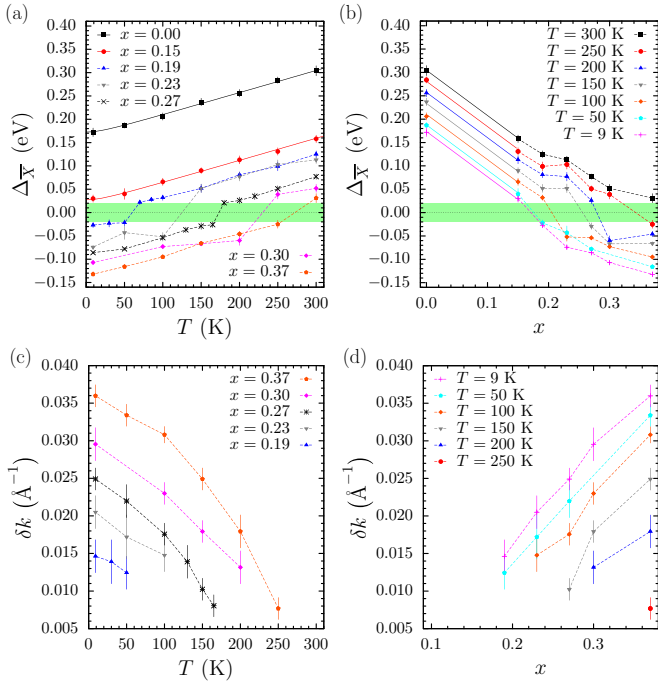


FIG. 2. (Color online) (a) Energy gap at \bar{X} as a function of temperature for $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ crystals with different tin contents x . The gap values have been determined from ARPES spectra as the ones shown in Fig. 1 [26]. In the TCI state, $\Delta_{\bar{X}}$ is taken to be negative. The green-shaded area represents the minimal gap that is always observed. The solid lines represent fits of Eq. (1) to the data. The dashed lines are merely guides to the eye. (b) Same data as in (a) but presented as a function of x . (c) Distance between \bar{X} and the surface-state band crossing in the TCI phase. (d) Same data as in (c) but presented as a function of x . The dashed lines are guides to the eye.

band edges determined by the local extrema in the dispersion along the high-symmetry directions. The determined band-edge positions are marked in Fig. 1 [26]. We correlate the formation of a metallic surface state with an inverted band structure which, following the usual convention, has a negative energy gap. The resulting temperature and tin-content dependencies are shown in Figs. 2(a) and 2(b), respectively. Concentrating first on the low- x samples ($x \leq 0.15$), we see that the band gap evolves nearly linearly as expected and commonly accepted. The data are very well described by the phenomenological model [31]

$$\Delta = E_0 + \alpha x + \sqrt{E_1^2 + (\beta T)^2}. \quad (1)$$

The values of the parameters are given in Table I and they are overall compatible with those found in the literature. However, when turning to the high- x samples, it is immediately

TABLE I. Parameters used in Eq. (1).

E_0 (meV)	E_1 (meV)	α (meV)	β (meV/K)	Ref.
130	0	-890	0.45	[11]
125	20	-1021	0.506	[31]
161(7)	12(9)	-969(20)	0.477(27)	This work

apparent that Eq. (1) does not hold anymore when the band gap becomes small and inverts. The curves for $x \geq 0.19$ all show a discontinuous band inversion, irrespective of the critical temperature [Fig. 2(a)] or the critical composition [Fig. 2(b)]. Moreover, the minimal observed absolute value of $\Delta_{\bar{X}}$ is about 20 meV to 25 meV and therefore slightly less but of the same order of magnitude as the smallest obtained laser energy [20]. Even though deviations from the approximately linear gap evolution were pointed out early on [20,31], models of type (1) are still widely in use and also stable gapless bulk states are yet postulated [32].

Before further discussing the observation of the discontinuous inversion, we would like to point out that the determination of the position of the gapped surface states in the normal-insulator case is somewhat hindered by the very low spectral weight at \bar{X} , where these states merge into the projected bulk states (cf. Fig. 1 and Ref. [21]). While this creates some uncertainty in the $\Delta_{\bar{X}}$ values in the normal state, our estimates—based on the continuous bands having a finite curvature—are overall conservative. Additionally, it appears as if occasionally the bottom of the conduction-band surface state is shifted away from \bar{X} , reminiscent of a “Rashba-like-split” surface state. Although we cannot exclude entirely that the shift in the normal band-insulator phase is merely an artifact of the missing spectral weight at \bar{X} , the rather clearly visible dispersion in the $x = 0.23$ high-temperature data indicates a real effect that so far cannot be reconciled with model calculations [16,18,21]. It is worth noting that for $(\text{Pb,Sn})\text{Te}$ recent calculations indicate a substantial influence of a finite surface potential gradient on the (111) surface states both in the TCI and the normal state [33]. Until similar calculations become available for the (001) surface, we only further quantify the separation of the Dirac points on the mirror line $\bar{\Gamma}$ - \bar{X} in the TCI state of $(\text{Pb,Sn})\text{Se}$. As shown in Figs. 2(c) and 2(d), the Dirac points move away farther from \bar{X} in the direction of $\bar{\Gamma}$ when the samples “advance deeper” into the TCI state, consistent with observations made previously for $(\text{Pb,Sn})\text{Te}$ [34].

Despite the above considerations, the observation of a nonlinear band evolution and the discontinuous inversion across the whole studied parameter range remains intact. Specifically, a linear gap evolution would suggest the high- x mixed crystals to be found in the TCI phase at room temperature. Yet, overall gapped surface states are observed. In addition, published ARPES data on $(\text{Pb,Sn})\text{Te}$ also suggest a similar discontinuous band inversion [cf. Fig. 3(d) of Ref. [34]]. So what is responsible for observing an open bulk band gap throughout all measurements? It seems that pure lattice dilatation effects play no role here, since computational studies of the pressure and strain dependence of the band gap and the topological transition in binary compounds yield a continuous basically linear inversion with a zero crossing of the gap [21,35]. However, when changing the temperature, the lattice dilatation constitutes only about half of the gap variation in the lead salts [7]. The other half is attributed to electron-phonon interactions [36]. Hence, lattice vibrations (and also mixed plasmon-phonon modes) are generally a grave factor when determining the accurate electronic structure in the studied materials and interband scattering becomes potentially important for small gap sizes. For degenerate semiconductors,

as they are studied here, carrier-carrier scattering also plays a role in the transport properties [37]. Therefore, interaction effects might not be entirely negligible. Finally, we emphasize that the nature of the band inversion is studied here in a solid solution. In such compounds disorder is always present and influences the electronic properties, although it does not hinder the transition into the TCI phase [38]. For example, “alloy scattering” is known to reduce the overall carrier mobility in mixed crystals compared to pure binary materials [9]. Only recently, an effort has been made to study the band inversion in (Pb,Sn)Te solid solutions by *ab initio* methods [39]. It was found that fully ordered structures exhibit semimetallic behavior, but that introducing short-range disorder leads to the formation of semiconductor band gaps, although still smaller than experimentally measured. Going beyond short-range disorder is, however, very computationally challenging.

Here, we propose a scenario for a band-inversion process in which the ZGS is essentially an unstable configuration for the system. The ZGS can generally be described by a band degeneracy forming a Dirac point. It is a general property of a Dirac point that, in the absence of symmetries protecting it, the spectrum easily becomes gapped [40]. In the bulk of $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$ there are no symmetries disallowing having a finite bulk gap at any value of the external parameters, such as x or T , even around the topological phase transition (TPT). As a consequence, although the bulk band gap necessarily has to be zero at some point, when evolving from a positive (topologically trivial state) to a negative (topologically nontrivial state) band gap, the ZGS itself can be essentially unstable and thus effectively not detectable in any measurement.

To demonstrate the instability of the ZGS within a simple model we use $\mathbf{k} \cdot \mathbf{p}$ theory near the bulk band-gap minima at any of the L points. There, the low-energy bulk Hamiltonian can generally be written as [8,13]

$$\mathcal{H} = m\sigma_z + v(k_1s_2 - k_2s_1)\sigma_x + v'k_3\sigma_y. \quad (2)$$

Here σ and s are Pauli matrices, with the eigenvalues of σ_z (± 1) labeling the cation (Pb or Sn) or the anion (Se) p orbitals, whereas the spectrum of s_3 (± 1) encodes for the Kramers (total angular momentum) degeneracy. The orthogonal coordinate system for the \mathbf{k} momentum vector has k_3 along Γ - L and k_1 aligned with the [110] direction perpendicular to the mirror plane. Moreover, the sign of the mass term m determines the topological nature of the material. The normal phase has $m > 0$, whereas for $m < 0$ the band structure is inverted and the material is in the nontrivial TCI phase. Note that there cannot be any symmetry protecting a ZGS ($m = 0$), since the $m\sigma_z$ mass term is always present in the Hamiltonian, on both sides of the TPT. The energy bands of the low-energy Hamiltonian Eq. (2) are doubly degenerate and given by $E = \pm \sqrt{v^2(k_1^2 + k_2^2) + v'^2k_3^2 + m^2}$, which forms an anisotropic Dirac spectrum with an energy gap equal to the mass m . Experimental evidence for massive bulk Dirac fermions in the

TCI phase has been reported by recent transport measurements [41]. Using the band structure we calculate the electronic free energy as a function of the mass m for the Hamiltonian in Eq. (2). We find that the free energy is reduced for a finite m compared to the $m = 0$ spectrum. Thus, with no symmetries disallowing a finite m and based on the electronic free energy, a finite energy gap is both allowed and energetically favorable. Equation (2) assumes an intrinsic system with the chemical potential in the middle of the bulk band gap. However, we find that adding a finite n -type doping, as evident in the experimental system, does not qualitatively change the free energy preference of the gapped system.

Thus, unlike in “true” zero-gap semiconductors [42], a perturbation of the system, such as potentially the aforementioned disorder, phonon, and interaction contributions, can lead to the stabilization of a fully gapped bulk state. This scenario implies a very sharp, or possibly even first-order, TPT, in which a finite energy gap is present in the bulk everywhere except in a very narrow region, where the gap quickly changes sign. In fact, the characteristic “flattening out” of a first-order transition of the energy gap as a function of the tuning parameter near the TPT is visible in the ARPES data in Figs. 2(a) and 2(b). First-order transitions between two topologically distinct phases have been previously predicted between a topological insulator and a Mott insulating phase in the presence of strong electron-electron interactions [43,44]. Our results suggest that sharp, and possibly even first-order, TPTs might not just be limited to strongly correlated electron systems. Thus, even if simple theoretical models, such as tight-binding approaches using the virtual crystal approximation (VCA) for solid solutions, seem to capture well the coarse features of the band inversion and the TPT [16,18,21], a more accurate description of the electronic state of the IV-VI narrow-gap semiconductors in the region where the fundamental band gap is of the order of a few tens of millielectronvolts is clearly needed. Such models would need to go beyond a static treatment of the crystal lattice and the VCA for solid solutions.

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- [26] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.90.161202> for the entire data set of this study.
- [27] Although the ($T = 300$ K, $x = 0.37$) data set contains an ambiguous EDC without an apparent gap close to \bar{X} , the overall band curvature indicates that the surface electronic structure is indeed gapped also in this case.
- [28] The data marked with a dagger [†, ($T = 9$ K, $x = 0.27$)] indicate a mass acquisition of the surface state at low temperatures, as previously observed in Ref. [29]. However, this does not affect the results of this Rapid Communication and further details shall be discussed elsewhere.
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