On the nature of the band inversion and the topological phase transition in (Pb,Sn)Se

B. M. Wojek,1,* P. Dziawa,2 B. J. Kowalski,2 A. Szczepiakow,1,2 A. M. Black-Schaffer,3 M. H. Berntsen,1,† T. Balasubramanian,4 T. Story,2 and O. Tjernberg1,†

1KTH Royal Institute of Technology, ICT Materials Physics, Electrum 229, 164 40 Kista, Sweden
2Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland
3Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden
4MAX IV Laboratory, Lund University, P.O. Box 118, 221 00 Lund, Sweden

(Dated: January 28, 2014)

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 Pb1−xSnxSe mixed crystals by means of angle-resolved photoelectron spectroscopy in the parameter space 0 ⩽ x ⩽ 0.37 and 300 K ⩾ T ⩾ 9 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.

PACS numbers: 71.20.-b, 71.70.Ej, 73.20.At, 79.60.-i

INTRODUCTION

Lead chalcogenides and related compounds have been studied intensely already in the second half of the last century [1]. These narrow-gap semiconductors are used for applications in infrared lasers [2] and detectors [3] as well as in thermoelectric devices [4, 5]. They also exhibit a large range of peculiar fundamental properties, such as positive temperature and negative pressure coefficients of the energy gap [6] and nonparabolic band dispersions [7]. Moreover, for suitable compounds and parameter ranges, the band gap undergoes an inversion (the parities at the top of the valence and the bottom of the conduction bands swap) as a function of temperature, pressure [8], and composition [9, 10]. At the interface between inverted and noninverted insulating layers gapless states were predicted to form [11]. 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 [12, 13] as well as the solid solutions (Pb,Sn)Te [14] and (Pb,Sn)Se [15]. In this state of matter, the mirror symmetry present in the rock-salt structure ensures degenerate energy eigenvalues along mirror lines, and hence metallic surface states on certain high-symmetry surfaces [16], when the band gap is inverted. Additionally, these topologically protected surface states exhibit Dirac-like dispersions and they are spin-momentum-locked [14, 17, 18].

Although the tunable band inversion in the lead and tin chalcogenides has been established for decades, the details of the gap closing remain in the dark. 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, to the best of our knowledge [19], a completely closed band gap (within the resolution of the respective measurement) has never been observed 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 [10] and very-low-energy laser emission seems to be hindered by plasmon-phonon excitations [8, 20].

The recent discovery of the TCI phase and the pertaining surface states has opened a new 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 X lie within the bulk band gap just beyond the valence and conduction-band edges projected from the bulk L points [12, 15, 17]. The same is true for the corresponding high-symmetry points of the (110) surface [16]. 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 article, we report on a systematic angle-resolved photoelectron spectroscopy (ARPES) study of (001)-oriented (Pb,Sn)Se mixed crystals. The topological phase boundary is established by the investigation of the evolution of the surface states around X as a function of composition and temperature. Moreover, contrary to the common theoretical expectations and the conclusions from previous experimental work, our observations point to an unstable zero-gap state in the bulk material. We compare our results with prior studies and discuss the implications for the band-inversion models of the IV-VI narrow-gap semiconductors.
EXPERIMENTAL DETAILS AND RESULTS

The n-type Pb$_{1-x}$Sn$_x$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 rock-salt structure (space group $Fm\overline{3}m$ [225]) both at room temperature and $T = 15$ K. The ARPES measurements in the temperature range $300$ K $\geq T \geq 9$ K have been conducted on samples cleaved along a (001) surface in ultra-high vacuum ($p \lesssim 6 \times 10^{-11}$ mbar before cleaving, $p \lesssim 5 \times 10^{-10}$ mbar after cleaving). The experiments have been performed using the laser-based ARPES set-up BALTAZAR equipped with a time-of-flight electron analyzer [23]. Linearly polarized light with a photon energy $h\nu = 10.5$ eV was used to excite the electrons. The total energy and crystal-momentum resolution was about 5 meV and better than 0.008 Å$^{-1}$, respectively.

The obtained ARPES spectra are shown in Fig. 1. The data in the vicinity of $X$ are plotted along the high-symmetry lines of the surface Brillouin zone $[\Gamma-X-M]$, cf. Fig. 2(a)]. In all spectra surface states are discernible. While the samples at high temperature ($T = 300$ K) exhibit gapped states for all $x$, at lower temperatures the spectra show a change from gapped surface states at low $x$ to metallic states crossing on the $\Gamma-X$ line at high $x$—the hallmark of the transition from a usual band insulator to a TCI. A closer inspection of the spectra shows that for $x \lesssim 0.15$, the energy gap at $X$ ($\Delta_X$) decreases when the temperature is lowered. The gap $\Delta_X$ also shrinks with increasing tin content when the samples are kept at room temperature. The opposite behavior is found for samples with high tin content at low temperatures.

As described in the introduction above, the surface-state dispersion can be viewed as an envelope of the projected bulk bands [cf. Fig. 2(b)]. Hence, $\Delta_X$ provides an estimate of the bulk band gap at $L$ [12, 15, 17] 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 tin content) 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 [6, 24].

ANALYSIS AND DISCUSSION

To gain a 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 $\Delta_X(x,T)$ in Fig. 2. The shown values represent the difference in the surface-state positions at the band edges determined by the local extrema in the dispersion along the high-symmetry directions. The individual positions are exemplarily marked in Fig. 1. 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(c) and 2(d), respectively. Concentrating first on the low-$x$ samples ($x \leq 0.15$), we see that the band gap evolves smoothly as expected and commonly accepted. The data are very well described by the phenomenological model [25]

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

The values of the parameters are given in Tab. I and they are overall compatible with those found in literature. However, when turning to the high-$x$ samples, it is apparent immediately that Eq. (1) does not hold anymore when the band gap becomes small and inverts. The curves for $x \gtrsim 0.19$ all show a discontinuous band inversion, irrespective of the critical temperature [Fig. 2(c)] or the critical composition [Fig. 2(d)]. Moreover, the minimal observed absolute value of $\Delta_X$ is about 25 meV and therefore of the same order of magnitude as the smallest obtained laser energy [20].

To compare our findings with reference values found in literature, we plot the infrared-absorption data of Ref. 10 in Figs. 2(c) and 2(f) together with the proposed gap dependencies of Refs. 10 and 25 (cf. Tab. I). Also here, clearly, the data for $x \leq 0.15$ are much better described by the phenomenological curves than the data for $x > 0.2$. For instance, in Fig. 2(f) the high-$x$ slope appears to be distinctively smaller than the low-$x$ slope (for both, positive and negative gaps), therefore naturally being inconsistent with the linear $x$ dependency in Eq. (1). Even though such deviations were pointed out early on [20, 25], models of type (1) are still widely in use and also stable gapless bulk states are yet postulated [26].

Before discussing our observation of the discontinuous inversion further, we would like to point out that the determination of the position of the gapped surface states in the normal-insulator case is hindered by the very low spectral weight at $X$, where these states merge into the projected bulk states (cf. Fig. 1 and Ref. 27).

| $E_0$ (meV) | $E_1$ (meV) | $\alpha$ (meV) | $\beta$ (meV/K) | Ref. |
|-------------|-------------|----------------|----------------|------|
| 130         | 0           | $-890$         | 0.45           | [10] |
| 125         | 20          | $-1021$        | 0.506          | [25] |
| 140(24)     | 28(28)      | $-934(40)$     | 0.524(76)      | this work |
While this creates some uncertainty in the $\Delta \Gamma$ values, our estimates are overall conservative. Additionally, it appears as if the bottom of the conduction-band surface state is shifted away from $\Gamma$. This shift is quantified in Figs. 2(g) and 2(h), where it is plotted together with the Dirac-point position in the TCI state. While the gapped-state shift is essentially constant for all studied samples and temperatures, the Dirac points move away further from $\Gamma$ in the direction of $\Gamma$ when the samples “advance deeper” into the TCI state, consistent with ob-

FIG. 1. ARPES spectra in the vicinity of $\mathbf{X}$ of the (001) surface of Pb$_{1-x}$Sn$_x$Se as a function of temperature (changing between different rows) and tin content $x$ (varying with the columns) [21]. Photons with an excitation energy $h\nu = 10.5$ eV have been used. The observed surface states display a transition from an overall gapped state (low $x$ or high $T$) to a state that is gapless along the $\Gamma$-$\mathbf{X}$ line (high $x$ and low $T$). Please observe that the energy scale changes with $x$. The distance between major (minor) tics on the axes of ordinates is chosen to be always 50 meV (10 meV) and the Fermi energies ($E_F = 0$) are aligned. On the abscissa the $\mathbf{X}$ positions are aligned. Their numerical values vary slightly with the changing lattice parameters. The white data points signify the surface-state (band-edge) positions at $\mathbf{X}$. Squares and diamonds are correlated with the $L_{sd}$ and $L_{sd}'$ character of the valence- and conduction-band edges, respectively.
sitions made previously for (Pb,Sn)Te [28]. Although, we cannot exclude entirely, that the shift in the normal band-insulator phase is merely an artifact of the missing spectral weight at \( \overline{X} \), 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 [15, 17, 27]. Notably, this observation is reminiscent of the normal-state behavior close to the topological phase transition found in the tunable topological-insulator system BiIr(S\(_{1-x}\)Se\(_{x}\))\(_2\) [29]. The latter effect also complicates the exact classification of metallic or gapped surface states in the transition region. For instance the \((x = 0.23, T = 100 \text{ K})\) data set could be classified both ways—without any influence on the following discussion.

Despite the increased uncertainty from the above considerations, the observation of a nonlinear band evolution and the discontinuous inversion remains intact. It is consistently found across the whole studied parameter range. 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, underlining once more the deviation from Eq. (1). In addition, also published ARPES data on (Pb,Sn)Te suggest a similar discontinuous band inversion [cf. Fig. 3(d) of Ref. 28], yet, this option was not further discussed at the time. 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 con-
tinuous basically linear inversion with a zero crossing of the gap \[27, 30\]. However, when changing the temperature, the lattice dilatation constitutes only about half of the gap variation in the lead salts \[6\]. The other half is attributed to electron-phonon interactions \[31\]. 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 inter-band scattering becomes potentially important for small gap sizes. For degenerate semiconductors, as they are studied here, also carrier-carrier scattering plays a role in the transport properties \[32\]. 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 \[33\]. For example, “alloy scattering” is known to reduce the overall carrier mobility in mixed the TCI phase \[33\]. For example, “alloy scattering” is known to reduce the overall carrier mobility in mixed crystals compared to pure binary materials \[8\]. Only known to reduce the overall carrier mobility in mixed crystals compared to pure binary materials \[8\]. Only recently, an effort has been made to study the band inversion in (Pb,Sn)Te solid solutions by ab initio methods \[34\]. 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 zero-gap state is essentially an unstable configuration for the system. The zero-gap state 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 the Dirac point, the spectrum easily becomes gapped \[35\]. In the bulk of Pb\(_{1-x}\)Sn\(_x\)Se there are no symmetries disallowing having a finite bulk gap at any value of the external parameters, such as \(x\) or \(T\). Thus nothing prevents the creation of an apparent avoided band crossing even around the topological phase transition. (This lack of symmetry protection for the bulk band degeneracy point in the zero-gap state should not be confused with the symmetry-protected surface-state Dirac spectra, which always appear in the presence of mirror-plane symmetry in the inverted band phase.) 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 non-trivial state) band gap, the zero-gap state itself can be essentially unstable and thus effectively not detectable in any measurement, even though the system clearly changes its topological state during the process.

To demonstrate the instability of the zero-energy state within a simple model we use \(k \cdot p\) theory near the bulk band gap minima at any of the \(L\) points. The low-energy bulk Hamiltonian can there generally be written as \[7, 12\]:

\[ \mathcal{H} = m_s \sigma_z + v(k_1 s_2 - k_2 s_1) \sigma_x + v'k_3 \sigma_y. \]  

Here \(\sigma\) and \(s\) are Pauli matrices, with the eigenvalues of \(\sigma_z\) \((\pm 1)\) labeling the cation (Pb or Sn) or the anion (Se) \(p\) orbitals, whereas the spectrum of \(s_3\) \((\pm 1)\) encodes for the Kramers (total angular momentum) degeneracy. The orthogonal coordinate system for the \(k\) momentum vector has \(k_3\) along \(\Gamma-L\) 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 topological crystalline phase (found at large \(x / \) small \(T\)). Note that there cannot be any symmetry protecting a zero-gap \((m = 0)\) state, since the \(m\) mass term is always present in the Hamiltonian, on both sides of the topological phase transition. The energy bands of the low-energy Hamiltonian Eq. \(2\) are doubly degenerate and based on the electronic free energy, as a function of the mass \(m\) of the band structure of Eq. \(2\) is reduced for a finite \(m\) compared to the zero-gap \(m = 0\) spectrum. Thus, with no symmetries disallowing a finite \(m\) and based on the electronic free energy, a finite energy gap is in fact both allowed and energetically favorable, even around the putative zero-gap phase transition point. The Hamiltonian Eq. \(2\) assumes an intrinsic system with the chemical potential in the middle of the bulk band gap. However, adding a finite \(n\)-type doping, as evident in the experimental system, does not qualitatively change the results.

Thus, unlike in “true” zero-gap semiconductors \[37\], a perturbation of the system, like 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, topological phase transition, in which a finite energy gap is present in the bulk everywhere except in a very narrow region, possibly point, where the gap quickly changes sign. In fact, the characteristic “flattening out” of a first-order transition of the energy gap as function of the tuning parameter near the topological phase transition is visible in the ARPES data in Figs. 2(c) through 2(f). First-order transitions between two topologically distinct phases have previously been theoretically predicted between a topological insulator and a Mott insulating phase in the presence of strong electron-electron interactions \[38, 39\]. Our results suggest that sharp, and possibly even first-order, topological phase transitions might not just be limited to strongly correlated electron systems. Thus, even if simple theoret-
tical models, such as tight-binding approaches using the virtual crystal approximation (VCA) for solid solutions, seem to capture the coarse features of the band inversion and the topological phase transition well [15, 17, 27], 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 meV is clearly needed. Such models would need to go beyond a static treatment of the crystal lattice and the VCA for solid solutions.

**SUMMARY**

To summarize, we have systematically studied the (001) surface states of (Pb,Sn)Se single crystals in the full rock salt substitution range and for temperatures between 9 K and 300 K by means of ARPES. The presented data establish the phase transition into the TCI state over an unprecedented parameter range. Furthermore, the evolution of the fundamental band gap of this semiconductor system has been investigated. Contrary to the expectations, our results provide indications that the anticipated gapless bulk state is essentially unstable during the band-inversion process. Instead, massive bulk states appear to be formed across the whole studied temperature and composition range.

We thank M. Sahlberg (Uppsala University) and M. Hudl (KTH Royal Institute of Technology) for supporting us with low-temperature powder X-ray diffraction measurements and A. V. Balatsky for stimulating discussions. This work was made possible through support from the Baltic Science Link project coordinated by the Swedish Research Council, the European Commission Network SemiSpinNet (PITN-GA-2008-215368), the European Regional Development Fund through the Innovation Network SemiSpinNet (PITN-GA-2008-215368), the Polish National Science Centre (NCN) Grant No. 2011/03/B/ST3/02659. P. D. and B. J. K. acknowledge support from the Knut and Alice Wallenberg Foundation, the European Commission Network SemiSpinNet (PITN-GA-2008-215368), the Polish National Science Centre (NCN) Grant No. 2011/03/B/ST3/02659. P. D. and B. J. K. acknowledge the support from the Baltic Science Link project coordinated by the Swedish Research Council, VR.

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* [http://bastian.wojek.de/](http://bastian.wojek.de/)

† Present address: Deutsches Elektronen-Synchrotron (DESY), Photon Science, Coherent X-ray Scattering, Notkestrasse 85, 22607 Hamburg, Germany

‡ oscar@kth.se

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