Band structure and topological phases of Pb$_{1-x-y}$Sn$_x$Mn$_y$Te by ab initio calculations

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The change in the composition of Pb$_{1-x-y}$Sn$_x$Te IV-VI semiconductor or in its lattice parameter can drive a transition from the trivially topological to the topological crystalline insulator (TCI), crossing a region where the alloy is in the Weyl semimetal phase. Incorporation of the magnetic Mn ions induces strong perturbations of the electronic structure, which act on both orbital and spin variables. Our first principles calculations show that the presence of Mn shifts the TCI and the Weyl region towards higher Sn contents in Pb$_{1-x}$Sn$_x$Te. When the Mn spin polarization is finite, the spin perturbation, like the orbital part, induces changes in band energies comparable to the band gap, which widens the Weyl area. The effect opens a possibility of driving transitions between various topological phases of the system by magnetic field or by the spontaneous Mn magnetization. We also propose a new method to calculate topological indices for systems with a finite spin polarization defined based on the concept of the Chern number. These valid topological characteristics enable an identification of the three distinct topological phases of the Pb$_{1-x-y}$Sn$_x$Mn$_y$Te alloy.

I. INTRODUCTION

Pb$_{1-x}$Sn$_x$Te and its selenide analogue, Pb$_{1-x}$Sn$_x$Se, are IV-VI narrow gap semiconductors known to undergo chemical composition, pressure or temperature driven band inversion accompanied by the transition from the trivial insulator to the topological crystalline insulator (TCI) phase.\(^1\)\(^-\)\(^4\) In contrast to (Bi,Sb)$_2$(Te,Se)$_3$ chalcogenide topological insulators, in TCIs it is the crystalline (mirror-plane) symmetry, not the time-reversal symmetry, that warrants the existence of the Dirac-like states on specific high symmetry crystal facets of bulk rock-salt crystals.\(^1\)\(^-\)\(^5\)\(^,\)\(^6\) Experimentally, the TCI surface states were observed by angle- and spin-resolved photoemission electron spectroscopy\(^2\)\(^-\)\(^4\)\(^,\)\(^7\)\(^-\)\(^9\), scanning tunneling microscopy/spectroscopy\(^8\), magnetotransport and magneto-optical quantum oscillatory effects.\(^9\)\(^-\)\(^11\) The band inversion and topological transition in Pb$_{1-x}$Sn$_x$Te was recently analyzed theoretically by ourselves\(^12\) and others\(^6\)\(^,\)\(^13\)\(^-\)\(^15\) using the density functional theory (DFT), the tight binding approximation (TBA), the virtual crystal approximation (VCA), and the method of special quasirandom structures (SQS) developed\(^16\) for the analysis of substitutional alloys. Confirming the successful basic picture obtained in early VCA calculations\(^6\) the other methods accounted for local chemical disorder, inevitably present in alloys. It was discovered that due to the splitting of the bands induced by locally varying crystal field symmetry there exists a transition region between the trivial and the TCI phase characterized by the zero energy gap\(^12\) with a possible Weyl semimetal type of energy bands arrangement.\(^13\)

In the quest for efficient ways of controlling the topological insulators and semimetals their alloying with other semiconductor materials proved very promising.\(^5\) Particularly interesting is alloying of TCIs with magnetic semiconductors, like MnTe or MnSe, thus combining the topological and magnetic properties of materials. Recent developments in the field of topological materials showed a rapid progress in ferromagnetic (FM) and antiferromagnetic (AFM) heterostructures expected to exhibit quantum anomalous Hall effect and topological magneto-electric effect.\(^5\)\(^,\)\(^17\)\(^,\)\(^18\) There exist several proposals for controlling topology in TCIs with nonzero magnetization as well for topological transition from the TCI to the Weyl semimetal (WSM) state.\(^19\)\(^-\)\(^22\) Pb$_{1-x}$Sn$_x$Te with Mn is known as IV-VI diluted magnetic (semimagnetic) semiconductor (DMS) exhibiting carrier-induced ferromagnetism driven by the Rudermann-Kittel-Kasuya-Yosida (RKKY) indirect exchange interaction via holes.\(^23\)\(^-\)\(^24\) As the solubility limit of Mn in bulk crystals of Pb$_{1-x}$Sn$_x$Mn$_y$Te is about 12 at. %, the ferromagnetic transition temperature observed in the bulk crystals is below 30 K.\(^24\)\(^-\)\(^26\) For thin epitaxial layers of topologically nontrivial terminal alloy, Sn$_{1-y}$Mn$_y$Te, the solubility appears smaller due to lower temperatures required for epitaxial growth, and the ferromagnetic Curie temperature is below 10 K.\(^22\)\(^,\)\(^27\) Importantly, Mn in Pb$_{1-x}$Sn$_x$Te substitutes Sn\(^{2+}\) or Pb\(^{2+}\) ions as isoelectronic Mn\(^{2+}\) ion with the configuration 3d\(^5\) and magnetic moment of 5 Bohr magnetons, as verified by electron paramagnetic resonance studies of both very diluted paramagnetic crystals\(^28\) and more concentrated ferromagnetic ones.\(^29\)

The influence of Mn ions on the band structure of quaternary system Pb$_{1-x-y}$Sn$_x$Mn$_y$Te and corresponding terminal ternary alloys Pb$_{1-y}$Mn$_y$Te and Sn$_{1-x}$Mn$_x$Te was studied to explain their very good thermoelectric parameters as well as ferromagnetic properties. It was found, both theoretically and experimentally, that the
key role is played by the band of heavy holes (Σ-band) and the position of its top with respect to the top of the highest valence band located at the L-point of the Brillouin zone. A good agreement was achieved between theoretical predictions and optical and thermoelectric data for the topologically trivial Pb$_{1-x}$Mn$_x$Te alloy: with the increasing Mn content the main gap at the L-point increases while the energy separation between the L- and the Σ-bands decreases. The calculated impact of Mn on the inverted gap in the trivial region, but to the decrease of the absolute value of the inverted gap in the TCI phase. This result is in agreement with experimental observations available for the trivial phase, e.g., in Pb$_{1-x}$Mn$_x$Te. The calculated impact of Mn on the inverted gap in the TCI phase is particularly relevant. Indeed, in this case analysis of experimental data (see, e.g., Ref. 37) is obscured by contradictory theoretical predictions, and the conclusions depend on the specific band structure models adopted in the interpretation.

II. TECHNICAL DETAILS OF CALCULATIONS

A. Modeling of disordered Pb$_{1-x-y}$Sn$_x$Mn$_y$Te crystals

Infinite Pb$_{1-x-y}$Sn$_x$Mn$_y$Te random mixed crystals are modelled by the $2 \times 2 \times 2$ supercells containing 64 atoms: 32 Te anions and 32 Pb, Sn or Mn cations. In the following, instead of Pb$_{1-x-y}$Sn$_x$Mn$_y$Te with the specified $x$ and $y$ we often use the notation Pb$_x$Sn$_y$Mn$_{32-y}$ where $k$, $l$, and $m$, $(k + l + m = 32)$, are the numbers of Pb, Sn and Mn atoms in the 64 atoms supercell, respectively. The most important problem is the choice of the spatial distribution of cations in the supercell, because, as we showed in Ref. 12 for Pb$_{1-x}$Sn$_x$Te, the band structure and in particular the energy gap $E_{gap}$ strongly depend on the cation configuration.

To solve this problem, we applied the SQS approach. The aim of this approach is to find such positions of different cations in the supercell that their distribution resembles a random distribution of cations in the infinite alloy as much as possible for several coordination spheres. However, for three different cations in the supercell, Pb, Sn and Mn, the number of their possible configurations is much larger than in the case of Pb and Sn only, thus the probability of finding the best possible SQSs is much smaller. In spite of this, as it will be seen in the following, although the calculated dependencies of energy gaps on the Sn concentrations are not perfectly smooth, general trends can be easily resolved.

For a given distribution of cations, the starting point of our analysis are the DFT calculations performed with the open-source OpenMX package. The calculations were done using the local density approximations with the Ceperly-Alder exchange-correlation functional. For Sn and Mn we used pseudopotentials distributed with the OpenMX (version 2013), for Pb and Te we used pseudopotentials with 4 and 6 valence electrons, respectively, generated previously using the program ADPACK distributed with the OpenMX. All the input parameters for calculations of pseudopotentials for Pb and Te were described in Ref. 30.

In the calculations we assume the experimental dependence of the lattice parameter on the chemical composition: $a = 6.460 - 0.145x - 0.558y$ Å. (1)

The experimental equilibrium Mn–Te bond length, $d_{Mn–Te} \approx 2.96$ Å, is much smaller than $d_{Pb–Te} \approx 3.23$ Å and $d_{Sn–Te} \approx 3.16$ Å. Consequently, the ions in the alloy do not occupy perfect NaCl lattice sites, and the internal distortions are of importance when considering the alloy band gap. We will show below that the hybridization between $3d$(Mn), $4s$(Mn) and $5p$(Te) orbitals...
has important influence on the energy gap. This effect depends on the distance between Mn and Te, making the geometry optimization necessary.

The energy gaps presented in the figures below are the minimal direct energy gaps on the \([111]\) direction in the 3D Brillouin zone (BZ). However, one should keep in mind that, contrary to PbTe or SnTe, due to lack of \(O_n\) local symmetry in most of the considered systems the smallest energy gaps are not, in general, placed on this direction (see the next section for an example).

The calculations are mostly done for systems containing even numbers of Mn ions in the supercell. With this choice one can study the impact of Mn doping on \(\text{Pb}_{1-x}\text{Sn}_x\text{Te}\) in the paramagnetic case, by assuming AFM spin configurations with the vanishing total spin, and separate the effects of spin polarization, modelled by assuming the FM spin configurations. In the latter case, the valence and conduction bands are spin-split, which in turn significantly affects the energy gaps, particularly when they are very small. Both situations are accessible experimentally, since the Curie temperature in the \(p\)-doped tin tellurides is of the order of 10 K.

### B. Calculations of topological indices

The OpenMX package enables to obtain TBA parameters for the TBA Hamiltonian. Using these parameters we calculate the necessary topological indices: the Chern numbers (CNs), the spin Chern numbers (SCNs), and the numbers \(C_{s+}\) and \(C_{s-}\). The method of calculation of \(C_{s+}\) and \(C_{s-}\) was described in Ref. 12. In short, the idea is to divide the valence band states for every \(k\) in the BZ into two sets, \(P_+(k)\) and \(P_-(k)\). In \(P_+(k)\) \((P_-(k))\) there are states with positive (negative) average spin. Taking the sums over \(k\) we obtain two vector bundles \(P_+ = \oplus_k P_+(k)\) \(P_- = \oplus_k P_-(k)\). Calculating the Chern numbers for these bundles we obtain \(C_{s+}\) and \(C_{s-}\). The spin Chern number \(SCN = (C_{s+} - C_{s-})/2\). The method of calculation of \(C_{s\pm}\) is based on the approach proposed by Fukui et al.\(^{44}\)

The microscopic Hamiltonian, i.e., the Pauli–Schrödinger Hamiltonian for electrons in \(\text{Pb}_{1-x-y}\text{Sn}_x\text{Mn}_y\text{Te}\) is time reversal invariant. However, after the DFT calculations the time reversal invariance is broken. The resulting spins of ions are finite and consequently the resulting TBA Hamiltonian’s have no time reversal symmetry. This feature was directly checked in a number of cases. Therefore, the general theorem that the Chern number calculated for a given 2D plane in the 3D BZ should be zero is not valid.

The BZ of our supercells is a cube. In the calculations of topological indices we use the \((001)\) plane crossing the \(k = (0,0,0)\) \(\Gamma\) point. This point corresponds to the \(L\) points of the unfolded BZ, and the main energy gap is situated at \(\Gamma\) or in its close vicinity.

The procedure for calculation of SCNs described previously\(^{12}\) can be applied directly to the systems without magnetic ions, or those containing an even number of magnetic ions in the supercell, arranged in such a way that their total magnetic moment vanishes. Then, the dimensions \(n_{\pm}(k)\) of \(P_{\pm}(k)\) are equal, \(n_{+}(k) = n_{-}(k)\). In the case when the total spin of the system is nonzero the procedure must be modified. In general, \(n_{+}(k) \equiv n_{+}\) and \(n_{-}(k) \equiv n_{-}\) are independent on \(k\), and they are related by \(n_{+}(k) = n_{-}(k) + N_S\) where \(N_S = 5(N_{\text{Mn}^1} - N_{\text{Mn}^4})\); exceptions are discussed below. Here \(N_{\text{Mn}^1}\) and \(N_{\text{Mn}^4}\) are the numbers of Mn atoms in the supercell with the spin up and down, respectively, and the factor 5 is related to the number of unpaired spins on the 3d(Mn) shell. Thus,

\[
 n_{-} = (n_{\text{val}} - N_S)/2 \quad n_{+} = (n_{\text{val}} + N_S)/2, \quad (2)
\]

where \(n_{\text{val}}\) is the number of occupied states. This is related to the exchange polarization of the bands due to nonvanishing net magnetization caused by Mn ions. Next, we divide the valence states into two subspaces and calculate Chern numbers \(C_{s+}\) and \(C_{s-}\).

This procedure was applied successfully in a vast majority of cases, however, for completeness, one should mention possible problems. Sometimes, the calculated \(C_{s+}\) and \(C_{s-}\) are noninteger. For example, for \(\text{Pb}_{31-n}\text{Sn}_{n}\text{Mn}_4\text{Te}_{32}\) meaningful results (integer \(C_{s\pm}\)) are obtained only for trivial and nontrivial regions, \(n \leq 9\) and \(n \geq 17\), respectively. In the transition region \(10 \leq n \leq 16\), where the values of the energy gaps are nearly zero, the procedure fails. This is related to the fact that in such cases there are a few points in the 2D plane of the BZ where the number of states with positive and negative average spins are not equal to \(n_{+}\) and \(n_{-}\) as in Eq. 2 but equal to \(n_{+} + 1\) and \(n_{-} - 1\), respectively. Thus it is impossible to build two vector bundles \(P_+\) and \(P_-\) of the dimensions \(n_{+}\) and \(n_{-}\), respectively and to calculate corresponding \(C_{s+}\) and \(C_{s-}\). The reason of those problems is the practically vanishing \(E_{\text{gap}}\). A detailed analysis shows that in the transition region the system is in the Weyl semimetal phase, and sometimes the Weyl’s nodes are at the plane in \(k\)-space used to calculate \(C_{s+}\) and \(C_{s-}\). Of course, for systems with \(E_{\text{gap}} = 0\) the calculations of CNs do not make sense. The example of \(\text{Pb}_{15}\text{Sn}_{16}\text{Mn}_4\text{Te}_{32}\) is discussed in the next Section.

### C. Calculations for Weyl semimetal region

The analysis of Weyl semimetal phase is not an easy numerical task because the zero energy gap points are grouped in the close vicinity of the \(\Gamma\) point in the supercell BZ. In the studied cases, all the Weyl nodes are contained in a cube of dimension 0.02 Å\(^{-1}\). In few cases we identified the points in the BZ where \(E_{\text{gap}} = 0\). However, in most cases we applied a much faster although less accurate method. Namely, the cube with the edge of 0.02 Å\(^{-1}\) was divided into 1000 smaller cubes with edges 0.002 Å\(^{-1}\). Next, for all small cubes we calculated the
BERY FLUX THROUGH THEIR FACES. OF COURSE, IN THIS PROCEDURE WE MISS THE CASES WHERE A PAIR OF WEYL NODES OF OPPOSITE CHARGES IS PRESENT INSIDE A SMALL CUBE.

III. RESULTS AND DISCUSSION

We begin with a brief summary of the main features characterizing the electronic structure of \( \text{Pb}_{1-x}\text{Sn}_x\text{Te}^{12} \) without \( \text{Mn} \) ions. They are presented in Fig. 1, which schematically shows the composition dependence of the band gap together with the relevant energies of the valence and conduction bands at the \( \Gamma \) point of the supercell BZ and the topological indices. With the increasing Sn content, \( E_{\text{gap}} \) changes the character from positive in \( \text{PbTe} \) to negative in \( \text{SnTe} \), Fig. 1a, driving the system from topologically trivial to TCI, which is also reflected in the non-vanishing spin Chern numbers in the Sn-rich \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \). Qualitatively different characters of the transition are obtained in the VCA and in the supercell method used in this paper. In the VCA, the chemical disorder of an alloy is absent, the system retains both the \( O_h \) point symmetry and the translational symmetry of the rock salt structure. As a result, the transition between topologically trivial and nontrivial phases is sharp, and takes place at a well-defined critical composition. In the supercell method, the alloy is simulated by the repeated supercells. The L points of the \( \text{PbTe} \) (or \( \text{SnTe} \)) Brillouin zone are folded to the \( \Gamma \) point of our 64-atom supercell BZ. After the folding, both the \( L_6^+ \)- and the \( L_6^- \)-derived bands of pure \( \text{PbTe} \) are 8-fold degenerate. These degeneracies are lifted in the presence of two types of cations because of the different chemical nature of \( \text{Pb} \) and \( \text{Sn} \), and of the disorder in their spatial distribution. This splitting is schematically shown in Fig. 1b. The magnitude of splittings and possible final degeneracies (e.g., double degeneracies in systems with inversion symmetry discussed below) depend on the actual distribution of \( \text{Pb} \) and \( \text{Sn} \) in the supercell. Consequently, in the supercell approach the trivial-TCI transition is smeared, there is a relatively wide composition window in which the band gap between occupied and unoccupied states vanishes, and the system is in the WSM phase,\(^{13}\) where topological indices are in general not defined. The energy of the \( L_6^- \) relative to the \( L_6^+ \) band extremum can also be reduced by application of the hydrostatic pressure. This closes the positive gap of \( \text{PbTe} \), opens the negative gap of \( \text{SnTe} \), and can drive the pressure-induced transition from the trivial to the TCI phase in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \). Again, the splitting of the energy levels leads to a smeared character of the transition, which proceeds through the Weyl phase (see Ref. 13 for details). In the VCA the transition is sharp, and the WSM phase is absent. Remarkably, the existence of semimetal region in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) was proposed based on recent experimental studies of temperature and composition dependence of conductivity.\(^{45}\)

A. \( \text{Comparison of Pb}_{30}\text{Sn}_{2}\text{Te}_{32} \) and \( \text{Pb}_{30}\text{Mn}_{2}\text{Te}_{32} \)

Mn ions in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) are magnetic and assume the high spin state \( S=5/2 \). The substitution of Mn for a cation introduces a perturbation acting on both the orbital and the spin variables, which in the following are referred to as the chemical and the spin part of perturbation, respectively. Both effects are analyzed here. The spin perturbation affects the band structure only when the Mn sublattice is spin polarized. Accordingly, we will assume a finite spin polarization of Mn (present in the FM phase, or induced by a weak magnetic field), but its influence on the orbital motion (including the Landau quantization) is neglected, because it requires a different approach to the band structure calculations, such as the effective mass model.

We first neglect the spin perturbation, and compare the impact of doping \( \text{PbTe} \) with \( \text{Sn} \) and \( \text{Mn} \). The comparison reveals the main features also present in the remaining cases. The results, obtained for a 64-atom \( \text{PbTe} \) supercell containing two \( \text{Sn} \) ions and that with two Mn ions with antiparallel spins, are presented in Fig. 2. The Figure shows the effect of hydrostatic pressure...
FIG. 2. (color online) Dependence on the lattice parameter $a$ of: (a), (b) energy gap, (c), (d) splitting of the $L_6^+$ and $L_6^-$ derived levels at the $\Gamma$ point of the supercell BZ, and (e), (f) the Chern numbers $C_{s+}$, $C_{s-}$. The left panel corresponds to Pb$_{30}$Sn$_2$Te$_{32}$, the right one to Pb$_{30}$Mn$_2$Te$_{32}$. $a_0$ is the equilibrium lattice parameter of PbTe.

(monitoring the decrease of $a$) on the electronic structure. The positions of Sn and Mn atoms in the supercells are the same, and the internal relaxations are neglected.

From Figs. 2a and 2b it follows that the incorporation of Mn ions to PbTe at equilibrium $a = a_0 = 6.46$ Å leads to the increase of the band gap from 0.20 eV for PbTe to 0.214 eV for Pb$_{30}$Mn$_2$Te$_{32}$, while the incorporation of Sn decreases $E_{gap}$ to 0.16 eV in Pb$_{30}$Sn$_2$Te$_{32}$ in accord with measurements.\textsuperscript{46,47} Considering the pressure dependence of the band gap we find that for both Pb$_{30}$Sn$_2$Te$_{32}$ and Pb$_{30}$Mn$_2$Te$_{32}$, $E_{gap}$ decreases with the decreasing lattice constant $a$ (i.e., with the increasing hydrostatic pressure), and eventually changes sign to negative, again in agreement with experiment.\textsuperscript{38,46–48} The pressure dependence of $E_{gap}$ shows regions where the band gap practically vanishes, and both systems are in the WSM phase. This effect was already pointed above, and is related to the alloy broadening, i.e., to the splitting of energy bands in mixed crystals. The splitting is shown in some detail in Figs. 2c and 2d. At the $\Gamma$ point of our 64-atom supercell BZ, the $L_6^+$- and $L_6^-$-derived bands of PbTe are 8-fold degenerate. These degeneracies are lifted in the presence of the Sn or Mn ions. Comparing the results for Pb$_{30}$Sn$_2$Te$_{32}$ and Pb$_{30}$Mn$_2$Te$_{32}$ we see that the level splittings, and thus the alloy broadening of the energy spectrum, is much larger in the latter case. This is because the substitution of Pb by a Group-II Mn ion generates a stronger crystal and electronic perturbation then the substitution of Pb by the isoelectronic Sn.

Finally, Figs. 2e and 2f show the topological indices
B. Influence of Mn on the band structure of Pb$\text{30}_{2}$Mn$\text{2}_{32}$ and Sn$\text{30}_{2}$Mn$\text{2}_{32}$.

The influence of Mn ions on the band structure of PbTe and SnTe is analyzed in Fig. 3, which shows the energy position of 8 highest valence bands and the 8 lowest conduction bands. As before, we use supercells with the lattice parameters taken according to Eq. 1, and containing two Mn ions. The Mn ions are placed at (0, 0, 0) and $a_0(1, 1, 1)$ in a perfect rock salt lattice neglecting the internal distortions. Thus, the Mn ions form a cubic body centered lattice, and the system has the $O_h$ symmetry. With this choice the wave functions are either even or odd with respect to inversion (like the wave functions of the $L_6$ band extrema in PbTe and SnTe), which makes the analysis more transparent. We mention that the calculated band gaps differ from those obtained with the SQS method, which reflects the dependence of $E_{\text{gap}}$ on the Mn distribution. The choice of supercells with an even number of Mn ions allows for separation of the effects induced by the chemical and the spin perturbation, which is achieved by comparing the FM and AFM spin configurations.

The final band structure of both systems is achieved in 4 steps. First, the pure compound is dilated or compressed to the appropriate lattice constant. In the second step, Mn ions are introduced to the supercell in the AFM spin configuration, but the atoms are not allowed to relax, which is denoted as the configuration I. We see that for both systems the Mn chemical perturbation induces splittings of the 8-fold degenerate band extrema by 0.1-0.3 eV, which is comparable to $E_{\text{gap}}$ of the PbTe and SnTe hosts.

In the third step, atoms relax to the configuration II, in which the nearest Te neighbors are moved towards the Mn ions along the bond directions, so that the Mn-Te bonds are reduced from 3.23 to 2.95 Å. The latter value is equal to that obtained after the geometry optimization and, in the case of Sn$_{1-x}$Mn$_x$Te is very close to the experimental one.$^{32}$ This effect leads to small changes in band energies. In the last step we assume the FM spin arrangement. Inclusion of the spin polarization reduces $E_{\text{gap}}$. In both PbTe and SnTe, the spin splittings are large, showing that the spin and the chemical perturbation are equally important, and can be comparable to the band gap.

Interestingly, as it follows from Fig. 3, the response to the Mn perturbation depends on the band symmetry. In particular, the spin splittings are considerably more pronounced in the case of the bands derived from $L_6^+$ than those derived from the $L_6^-$ band extrema, independent of the host and of the valence or conduction band character. We relate this result with the atomic orbitals composition of the corresponding wave functions. In the case of Pb$\text{30}_{2}$Mn$\text{2}_{32}$, the wave function of the VBM are even with respect to the inversion symmetry operation. They contain contributions from the $3d$(Mn) orbitals, and these contributions are larger for the configuration II then for the configuration I. This is due to the stronger hybridization of $3d$(Mn) with $p$(Te) after the lattice relaxation, when the Mn-Te bonds are shorter. The wave functions of the $L_6^-$-derived conduction levels are odd with respect to the inversion, and practically do not contain the Mn orbitals and do not respond to the Mn presence. The situation is different in Sn$\text{30}_{2}$Mn$\text{2}_{32}$. The wave function of the VBM are odd and do not contain the Mn orbitals. The wave function of the lowest valence level shown in the Fig. 3 is even with respect to inversion and contains the $4s$(Mn) orbital. The wave functions of the conduction states are even. The first conduction level contains $4s$(Mn), while the higher three levels contain the $3d$(Mn) orbitals.
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The above results, together with those for the sup-
cells with 4 Mn ions with 3 spins up and one spin down,
enough.

In spite of that problem, two qualitative effects should be
noticed. First, we find that as a result of the Mn-
induced change of $E_{\text{gap}}$ in Pb$_{1-x-y}$Sn$_x$Mn$_y$Te the trivial-
to -nontrivial transition region is shifted to higher con-
centrations of Sn. Our calculations indicate that for Pb$_{1-x}$Sn$_x$Te the energy gap vanishes for $x \approx 0.35$, what corresponds quite well to the experimental values $x \approx 0.4$. For Pb$_{1-x-y}$Sn$_x$Mn$_y$Te with $y \approx 0.06$, $E_{\text{gap}} = 0$
for a higher $x \approx 0.5$, but the precise experimental value is not known.

Second, since adding Mn enhances alloy broadening, one
would expect that the region of the Weyl phase is wider in Pb$_{1-x-y}$Sn$_x$Mn$_y$Te then in Pb$_{1-x}$Sn$_x$Te. Paradoxically,
the calculated $E_{\text{gap}}(x)$ dependence exhibits an opposite
effect, and in the case of 4 Mn ions in the supercell the Weyl
phase is practically absent. This effect is ascribed to the fact that the splittings of both the VBM and CBM
significantly increase with the increasing Mn concentration.
This is illustrated in Fig. 5, which presents the
energies of the 8 highest valence states and the 8 lowest
conduction states at $\Gamma$ as a function of the Sn concen-
tration in Pb$_{1-x-y}$Sn$_x$-Mn$_y$Te containing two and four Mn ions in the supercell. Indeed, in the case of Pb$_{1-x}$Sn$_x$Te the spread
is the smallest, the levels are almost degenerate, which
is reflected in the wide composition window of the Weyl
phase. On the other hand, in the case of 4 Mn the spread
of the levels is substantial, their energies are well resolved,
and the transition is sharp.

The strong chemical disorder may also be the cause
why the Weyl phase is usually not observed in exper-
iment, with the exception of one work, in which crystals
with extremely low carrier concentrations were used. In
actual alloys, apart from the chemical disorder, there are
also native defects, mostly vacancies, what increases the
disorder and can lead to larger band splittings.

We now turn to the impact of the spin polarization
on energy levels in Pb$_{1-x-y}$Sn$_x$Mn$_y$Te. It was shown in
detail in Fig. 3 for PbTe and SnTe with 2 Mn ions constit-
tuting BCC lattice. Figure 6 compare the composition
dependence of the band gap for different spin configu-
rations for Pb$_{1-x-y}$Sn$_x$Mn$_y$Te containing two and four manganese atoms in the supercells. In the FM configu-
ration, the spin splittings of the VBM and CBM induce
a considerable reduction of the absolute value of $E_{\text{gap}}$.

As a consequence of spin polarization, in the case of al-
loys with 2 Mn ions the Weyl region characterized by $E_{\text{gap}} = 0$ is 3 times wider than that in the AFM case.

In the case of 4 Mn in the supercells, the effect is even
dramatic, since $E_{\text{gap}}$ vanishes for all composition
$x > 0.25$. Indeed, this is in sharp contrast with the very
narrow composition window calculated in the absence of
spin polarization. These results are in qualitative agree-
ment with those of Ref. 19, which also finds that the
width of the Weyl region increases with the spin polar-
ization of magnetic ions.

C. Supercells with 0, 2 or 4 manganese ions

In this section we analyze the dependence of the energy
gap and topological properties of Pb$_{1-x-y}$Sn$_x$Mn$_y$Te on
the Sn concentration. The impact of Mn is revealed by
comparing three cases: that with no Mn, $y = 0$, with
$y = 0.0625$, and with $y = 0.125$, which corresponds to
$0, 2$, and 4 Mn atoms at the cation sites of a 64-atom
supercell, respectively. We begin with the antiferromag-
netic configuration of Mn spins. In Fig. 4 we show $E_{\text{gap}}$
and the corresponding topological indices as the function
of the Sn concentration. The increase of $E_{\text{gap}}$ with the
increasing Mn content in PbTe was analyzed above. As
we pointed out, doping PbTe with Mn lowers the energy
of the $L_6^+$ band relative to the $L_6^-$ band, thus increasing
the band gap. In SnTe this effect takes place as well, but in this case it decreases the inverted $E_{\text{gap}}$. As it follows
from Fig. 4, this effect of Mn persists also in the
Pb$_{1-x-y}$Sn$_x$Mn$_y$Te alloy in the whole composition range.
While the decrease of energy of $L_6^+$ relative to that of $L_6^-$
induced by 2 and 4 Mn ions in the supercells is clear for all Sn concentrations, it is not always possible to distin-
guish the results for 2 and 4 Mn ions. This problem stems
from the fact that the differences in band energies, and in particular the band gap itself, are smaller than the fluctua-
tions inherent to our approach. Indeed, they could be
got rid of by averaging over a substantially larger number
of atomic configurations in the supercells. Apparently, in
this specific case, the SQS approximation is not accurate

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{(color online) Dependence on the number of Sn ions in
the supercell of: (a) the energy gaps, (b) the spin Chern number $C_s$
for Pb$_{32-n}$Sn$_n$Te$_{32}$ (dots), for Pb$_{30-n}$Sn$_n$Mn$_2$Te$_{32}$
(triangles) and Pb$_{28-n}$Sn$_n$Mn$_4$Te$_{32}$ (stars).}
\end{figure}
FIG. 5. (color online) Dependencies of 16 energy levels nearest to the Fermi energy at the Γ point of the supercell BZ for different Mn concentrations. The closed symbols represent the levels with the wave functions dominated by the $5p$ orbitals (L$_6^+$ derived states), and the open symbols correspond to those dominated by the cation $p$ orbitals (L$_6^−$ derived states). Thick black lines show the energy position of the VBM.

FIG. 6. (color online) Dependence of the energy gap on the spin polarization for supercells containing (a) 2 Mn and (b) 4 Mn atoms. Orientations of Mn spins and spin configurations are shown by arrows. Thick horizontal lines denote the regions of the Weyl semimetal phase, WSM, where the number of Weyl nodes is nonzero. n is the number of Sn atoms in the supercell.
allow for a few quasi-quantitative conclusions. Namely, in the case of PbTe, incorporation of two Mn ions in the AFM state rises $E_{\text{gap}}$ by 0.03 eV, while their spin polarization lowers $E_{\text{gap}}$ by about the same amount. Thus, the presence of 2 Mn in the FM configuration leaves the band gap unchanged, which illustrates well our earlier conclusion that the chemical and the spin perturbations are equally important. The analogous result holds in the case of 4 Mn ions in supercells. The results for the intermediate case of 4 Mn ions with 3 spins up and one spin down are fully consistent with this picture.

In previous works, the trivial-to-TCI phase transition was induced by either the change of composition of Pb$_{1-x}$Sn$_x$Te or by hydrostatic pressure. The results of Figs. 4 and 6 point out to a very interesting possibility of driving the transition by applying magnetic field. Indeed, in the case of Pb$_{1-x}$Sn$_x$Te with composition $x=0.25$ with 4 Mn ions, $E_{\text{gap}} = 0.1$ eV in the paramagnetic case, i.e., in the AFM configuration, but vanishes in the FM configuration. Such a scenario is also discussed in Ref. 19.

### D. The Weyl semimetal phase

A detailed characterization of the Weyl semimetal phase is provided by Table I, where we list the positions of Weyl’s nodes in the $k$ space, the corresponding energy gaps, topological charges, and the energies of the nodes for Pb$_{15}$Sn$_{16}$Mn$_1$Te$_{32}$. The vanishing $E_{\text{gap}}$ makes it impossible to calculate the topological indices, as it was discussed in Section II.

As it is shown in Fig. 7, the analysis of the Weyl’s nodes helps to define more precisely the transition region between the trivial and the TCI phase. In the case of 4 Mn ions in the supercell we find only one Sn concentration, $n = 18$, for which the number of Weyl’s nodes is nonzero. This confirms the fact that for larger concentrations of Mn the Weyl region is very narrow, or is just absent.

Finally, as additional example, we analyzed the number of Weyl’s nodes as the function of the lattice parameter for Pb$_{1-x-y}$Sn$_x$Mn$_y$Te containing one Mn ion in the supercell. The results are presented in Fig. 8. They show that the number of Weyl’s nodes provides a precise measure of the width of the Weyl region.

### IV. CONCLUSIONS

With the increasing Sn content in the Pb$_{1-x}$Sn$_x$Te alloy, a transition from the topologically trivial to the non-trivial topological crystalline insulator (TCI) phase takes place. The transition is smeared, because there is a wide composition window, in which the alloy has the zero band gap and remains in the Weyl semimetal phase. The calculated critical Sn concentration corresponding to the onset of the transition of Pb$_{1-x}$Sn$_x$Te to the Weyl phase, $x = 0.3$, is reasonably close to that experimentally observed. The Weyl phase extends from 0.3 to 0.5, and for higher $x$ the alloy assumes the TCI phase.

Using ab initio calculations we investigate consequences of alloying Pb$_{1-x}$Sn$_x$Te with Mn. The group-II
Mn is chemically different from the Pb and Sn group-IV cations, and thus it introduces a strong chemical perturbation of the Pb$_{1-y}$Sn$_y$Te electronic structure. Next, Mn in the IV-VI compounds is in the high spin state, perturbation acting on spin variables of band carriers is present when the macroscopic spin polarization of Mn ions is finite. The main conclusions are as follows.

1. At higher temperatures, the system is paramagnetic with the vanishing spin polarization. In this case, the incorporation of Mn ions into Pb$_{1-y}$Sn$_y$Te leads to the increase of $E_{gap}$ on the PbTe side and its decrease on the SnTe side, which modifies the composition window of the Weyl phase. For example, in the presence of Mn, the Weyl area shifts from $y = 0$ to $y = 0.5$. When the Mn ions are fully spin polarized, the Weyl area extends from $y = 0.5$ to 1.0.

2. The strong impact of the spin polarization on the energy bands opens an interesting possibility of inducing a transition from the trivial to the Weyl phase by magnetic field or by spontaneous magnetization. The effect is expected to occur for $x > 0.35$.

3. Pb$_{1-x-y}$Sn$_x$Mn$_y$Te alloys can be characterized by topological indices, which are based on the concept of the Chern number. If the total spin polarization of the Mn ions vanishes, the spin Chern number constitutes the appropriate topological index. In other cases, the alloy can be characterized by two indices, $C_x$ and $C_y$. The dependencies of $E_{gap}$ on the Sn content or on the lattice parameter agree very well with the corresponding dependencies of our topological indices. Thus, they constitute a valid characteristics of the system, and in particular they reveal whether $E_{gap}$ is positive or negative.

4. In the semimetal Weyl phase, the Weyl’s nodes are placed very close in the $k$ space ($\sim 0.02$ Å$^{-1}$), thus the observation of the splitting of Dirac cones using ARPES technique is rather not possible at present.

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References

25. P. Lazarczyk, T. Story, M. Arciszewska, and R. R. Galążka, J. Magn. Magn. Mater. 169, 151 (1997).
26. G. P. Mazur, K. Dybko, A. Szczepakow, J. Z. Domagala, A. Kazakov, M. Zgirski, E. Łusakowska, S. Kret, J. Koczak, T. Story, M. Sawicki, and T. Dietl, Phys. Rev. B 100, 041408(R) (2019).
27. A. J. Nadolny, J. Sadowski, B. Taliashvili, M. Arciszewska, W. Dobrowolski, V. Domukhovski, E. Łusakowska, A. Mycielski, V. Osinniy, T. Story, K. Świątek, R. R. Galążka, and R. Diduszko, J. Magn. Magn. Mater. 248, 134 (2002).
28. T. Story, C. H. W. Swüste, P. J. T. Eggenkamp, H. J. M. Swagten, and W. J. M. de Jonge, Phys. Rev. Lett. 77, 2802 (1996).
29. T. Story, P. J. T. Eggenkamp, C. H. W. Swüste, H. J. M. Swagten, W. J. M. de Jonge, and A. Szczepakow, Phys. Rev. B 47, 227 (1993).
30. A. Łusakowski, P. Bogusławski, and T. Radzyński, Phys. Rev. B 83, 115206 (2011).
31. M. Bukala, P. Sankowski, R. Buczko, and P. Kacman, Phys. Rev. B 86, 085205 (2012).
32. X. Tan, H. Shao, T. Hu, G.Q. Liu, S. F. Ren, J. Phys.: Condens. Mat. 27, 095501 (2015).
33. G. Tan, F. Shi, S. Hao, H. Chi, T.P. Bailey, Li-Dong Zhao, C. Uher, C. Wolverton, V.P. Dravid, and M. G. Kanatzidis, J. Am. Chem. Soc. 137, 11507 (2015).
34. J. He, X. Tan, J. Xu, G.Q. Liu, H. Shao, Y. Fu, and J. Jiang, J. Mat. Chemistry A 3, 19074 (2015).
35. X.J. Tian, H.Z. Shao, J. He, C.Q. Liu, J.T. Xu, J. Jianmg, and H.C. Jiang, Phys. Chem. Chem. Phys. 18, 714 (2016).
36. Y. Liu, S. K. Bose, and J. Kudrnovský, J. Magn. Magn. Mat. 375, 15 (2015).
37. P. Lazarczyk, M.V. Radchenko, G.V. Lashkarev, T. Story, K. Dybko, and R. R. Galążka, Semicond. Sci. Technol. 13, 980 (1998).
38. G. Bauer, H. Pascher, and W. Zawadzki, Semicond. Sci. Technol. 7, 703 (1992).
39. see http://www.openmx-square.org
40. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
41. S. Miotkowska, E. Dynowska, I. Miotkowski, A. Szczepakow, B. Witkowska, J. Kachniarz, and W. Paszkowicz, J. Crystal Growth 200, 483 (1999).
42. R. J. Iwanowski, W. Paszkowicz, K. Ławniczak-Jabłońska, M. H. Heinonen, B. Witkowska, and J. Feldhaus, Chem. Phys. Lett. 336, 226 (2001).
43. E. Prodan, Phys. Rev. B 80, 125327 (2009).
44. T. Fukui, Y. Hatsugai, and H. Suzuki, J. Phys. Soc. Jpn. 74, 1674 (2005).
45. C-L Zhang, T. Liang, N. Ogawa, Y. Kaneko, M. Kriener, T. Nakajima, Y. Taguchi, and Y. Tokura, Phys. Rev. Materials 4, 091201(R) (2020).
46. G. Nimtz and B. Schlicht, Narrow Gap Semiconductors in Springer Tracts in Modern Physics Vol. 98 (ed. Höhler, G.) (Springer-Verlag, Berlin, 1983).
47. D. R. Khokhlov, (ed.) Lead chalcogenides: physics and applications, (Taylor and Francis, New York, 2003).
48. J. Niewodniczańska - Zawadzka, and A. Szczepakow, Solid State Commun. 34, 887 (1980).
49. T. Liang, S. Kushwaha, J. Kim, Q. Gibson, J. Lin N. Kioussis, R. J. Cava, and N. P. Ong, Sci. Adv. 3, e1602510 (2017).