Topological crystalline insulator states in Pb$_{1-x}$Sn$_x$Se

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S1 Crystal growth, structural and chemical characterization.
The method of self-selecting vapour growth (SSVG) was applied to manufacture Pb$_{0.77}$Sn$_{0.23}$Se monocrystals (Supplementary Fig. 1) of excellent crystal structure as well as chemical homogeneity. The SSVG method is particularly suitable for optimisation of the latter because the crystals grow in a near-equilibrium regime. Moreover, the temperature profile set in the technological furnace ensures growth of a crystal in exclusive contact with its source material. In the case of the considered alloy, the method allows controlling deviations from stoichiometry to achieve (without heterodopants) the required n-type conductivity with a moderate electron concentration. The SSVG method was successfully employed by one of us (A.S.) to grow monocrystals of various II-VI and IV-VI semiconductor compounds and their solid solutions [26,27].

X-ray diffractometry (XRD) analysis of the crystal structure of Pb$_{1-x}$Sn$_x$Se was done at room temperature for both as-grown and freshly cleaved (001) crystal surfaces as well as for powdered polycrystals. It revealed the rock-salt single-crystal phase with a lattice parameter $a = (6.0979 \pm 0.0006)$ Å corresponding to a Sn content of $x = 0.228 \pm 0.005$ [22]. XRD rocking-curve measurements of the (002) diffraction peaks yield a full width at half maximum parameter $\Delta \omega = (70$ to $150)$ arcsec for various (001) surfaces. The chemical composition of the crystals was determined by energy-dispersive X-ray spectroscopy (EDX) using a scanning electron microscope SEM Hitachi SU-70 equipped with a Thermo Scientific NSS7 microanalysis system. Probing different places (over an area of 1 mm$^2$) of a sample freshly cleaved (in air) we found a Sn content of $x = 0.234 \pm 0.005$.

Supplementary Figure 1.
As-grown Pb$_{0.77}$Sn$_{0.23}$Se bulk monocrystal. The mirror-like planes at the front part of the crystal are natural (001) facets of a rock-salt-type crystal.
The surface morphology of Pb$_{0.77}$Sn$_{0.23}$Se crystals was studied using a Dimension Icon Atomic Force Microscope (AFM). The measurements were carried out for (001) surfaces prepared by cleaving the crystals in air at room temperature. Supplementary Fig. 2 presents an AFM image for an area of 1×1 μm$^2$ and the section analysis taken along the indicated line. The root-mean-square surface roughness parameter for this area equals 6.8 Å (i.e., about just one lattice parameter). The freshly cleaved (001) surface consists of large atomically flat regions with small vertical steps with heights of a few monolayers. Time–dependent AFM measurements of a cleaved surface exposed to air showed substantial surface contaminations appearing after 1.5 hours.

Supplementary Figure 2.
Morphology of the (001) surface of a Pb$_{0.77}$Sn$_{0.23}$Se crystal. Atomic force microscopy (AFM) image of a (001) surface of a bulk crystal freshly cleaved in air at room temperature. The height differences between the points marked with green and red arrows equal 6.8 Å and 11.5 Å, respectively. The macroscopically large region between the black arrows is atomically flat.

S2 Angle-resolved photoemission measurements at various photon energies.
Supplementary Fig. 3 shows three sets of selected constant-energy surfaces for Pb$_{0.77}$Sn$_{0.23}$Se, in the vicinity of the $\bar{X}$ point, measured at a temperature of 110 K using photon energies of 17.5 eV, 25 eV, and 40 eV with corresponding overall energy resolution of 25 meV to 40 meV. The data were acquired at the I4 beam line of the MAX III synchrotron at MAX-lab, Lund University, Sweden. As seen in the figure, the spectral weight is shifted when changing the photon energy. For the measurements at 25 eV and 40 eV the part of the surface state located in the second Brillouin zone (BZ) is the most intense. At a photon energy of 17.5 eV the most intense part shifts from the first BZ for high binding energies (below the Dirac points) to the second zone for lower binding energies (above the Dirac points). Apart from these intensity variations the position of the Dirac-like feature with respect to the surface Brillouin zone is independent of photon energy (within the limits of experimental accuracy) suggesting that the observed feature is indeed a surface electronic state.
Comparing energy-momentum slices from the data sets taken at different photon energies also confirms that the feature has virtually no photon-energy dependence. Supplementary Fig. 4 displays such energy-momentum slices through the Dirac point located in the first surface BZ (analogous to Fig. 3a in the main text) for the photon energies 10.5 eV, 17.5 eV, 25 eV and 40 eV. The cuts are parallel to the $\overline{M} - \overline{X} - \overline{M}$ direction. The 10.5 eV data are taken at the BALTAZAR laser ARPES facility at a temperature of 100 K and the 17.5 eV, 25 eV and 40 eV data are acquired at the I4 beam line of MAX III at a temperature of 110 K. Disregarding for the moment the intensity differences, a clear X-shaped state is seen for all photon energies. However, for the 17.5 eV data the Dirac point is shifted about 55 meV towards lower binding energy as compared to the 10.5 eV measurement. A slight further shift towards lower binding energy is observed for the other measurements. The 10.5 eV data were recorded within 12 hours after cleaving whereas the 17.5 eV, 25 eV and 40 eV data were recorded at 80 hours, 85 hours and 100 hours post cleaving, respectively. Thus, the shift in binding energy is likely related to the aging of the surface due to residual gas adsorption. Similar observations have previously been made for topological insulators, e.g. Bi$_2$Se$_3$, for which the Dirac point shifts towards higher binding energy upon gas adsorption and these shifts can amount to several hundred millielectronvolt [P.D.C. King et al., Phys. Rev. Lett. 107, 096802 (2011)]. In the present case, the shift is towards lower binding energy and seems at first glance to be of smaller magnitude. In the Bi$_2$Se$_3$ case, the adsorption of residual gas is accompanied by the appearance of quantum well states that display a large Rashba split [P.D.C. King et al., Phys. Rev. Lett. 107, 096802 (2011)]. For Pb$_{0.77}$Sn$_{0.23}$Se, neither the laser-based data nor the synchrotron data show any clear sign of quantum well states or other additional surface-related states.

Employing a free-electron model with an inner potential of 15 eV deduced from normal emission data, for states close to the Fermi energy at $\overline{X}$ the photon energies 10.5 eV, 17.5 eV, 25 eV and 40 eV correspond to $k_z$ values 2.2, 2.5, 2.9 and 3.4 (in units of $2\pi/a$, where $a = 6.075$ Å), respectively. However, it should be kept in mind that the $k_z$ resolution in the studied photon-energy range is very limited as a consequence of the high surface sensitivity. Nevertheless, different $k_z$ values are probed and bulk-related dispersive features are expected to differ. The lack of dispersive differences for the Dirac state between the data sets once more confirms the surface nature of the observed state.
Looking in more detail at the intensity “inside” the Dirac state it is clear from Fig. 3 in the main text that this intensity in the 10.5 eV data is partially originating from the “second cone”, which has its Dirac point located on the other side of $\bar{X}$. This is not the case for the higher photon energy measurements since the shift of the chemical potential causes this contribution to lie above the Fermi level. However, from Supplementary Fig. 4 it is apparent that bulk features contribute to the intensity “inside” the cone since it changes as a function of photon energy. The Fermi level intensity varies with photon energy as does the intensity close to $k_y = 0$ for high binding energies. The high intensity at the Fermi level in the 17.5 eV data and at higher binding energy in the 25 eV data might indicate that the corresponding points in reciprocal space are close to a conduction-band minimum and a valence-band maximum, respectively, although final-state effects and the limited $k_z$ resolution hinder a more accurate determination.

Returning to the Dirac state, looking at the intensity variations between the different photon energies one observes that the expected increase in intensity at the Dirac point (c.f. Fig. 3a in the main text), due to the band crossing, is not present. This indicates that the gap is not yet fully closed and that the transition temperature is below 100 K. The 17.5 eV data seems to indicate a closed gap but caution is called for since intensity variations as a function of photon energy might mask a small gap. Such variations are clearly present since at 10.5 eV the main intensity is in the part above the Dirac point whereas the opposite is true for 40 eV. Also, the intensity at the Dirac point is varying across the photon energies used. The difference in energy resolution between the laser ARPES and synchrotron measurements provides another potential explanation for the apparently closed gap in the higher photon energy data.

![Supplementary Figure 4](image)

**Supplementary Figure 4.** Energy-momentum slices across the surface Dirac cones in Pb$_{0.77}$Sn$_{0.23}$Se taken at the photon energies 10.5 eV, 17.5 eV, 25 eV and 40 eV.

**S3 Electrical properties.**

The samples for electron transport measurements were prepared from as-grown bulk crystals by cleaving along three mutually orthogonal (001) planes to get standard parallelepiped Hall-bars of typical dimensions 2x2x7 mm$^3$. Directly after cleaving, six contacts were made by soldering with indium. The low-field ($B = 0.5$ T) Hall effect and resistivity measurements were performed in a continuous-flow helium cryostat with a DC current of 50 mA applied along the [100] crystallographic direction. The electron transport parameters (resistivity, Hall electron concentration and Hall mobility) presented in Supplementary Fig. 5 were obtained considering one transport channel only in the analysis, as usually done for characterisation purposes.
S4 High-field magnetotransport measurements.
The high-field measurements of the resistivity tensor components $\rho_{xx}$ and $\rho_{xy}$ were carried out in a liquid-helium cryostat equipped with a $B = 13$ T superconducting solenoid. The magnetoresistance presented in Supplementary Fig. 6a is of usual orbital origin with characteristic two-carrier conductivity contributions. Supplementary Fig. 6b displays the as-measured experimental data for the transverse $\rho_{xy}$ tensor component, which after the subtraction of linear terms were transformed to the $\Delta \rho_{xy}$ curves shown in Supplementary Fig. 6c.

The experimentally observed magnetic field nonlinearities in the $\rho_{xy}$ tensor component and the non-quadratic magnetoresistance indicate the presence of at least two parallel conduction channels. The dominant conduction channel can be identified as a bulk conduction band contribution. The identification of the other electronic channel needs further magnetotransport studies, in particular for samples with lower bulk electron concentration.

Supplementary Figure 5.
Electrical characterisation of Pb$_{0.77}$Sn$_{0.23}$Se crystals. Temperature dependence of the resistivity (a), the Hall electron concentration (b), and the Hall electron mobility (c) determined from low-field classical transport measurements.

Shubnikov-de Haas oscillations.
The good electrical quality of the Pb$_{0.77}$Sn$_{0.23}$Se crystals reflected in the high electron mobility permits the experimental observation at very low temperatures of quantum oscillations of the magnetoresistance (the Shubnikov-de Haas effect, SdH). The SdH oscillations in $n$-Pb$_{0.77}$Sn$_{0.23}$Se displayed in Supplementary Fig. 7 are of bulk (3D) origin. This was confirmed in a tilted-field experiment, where the magnetic-field positions of the oscillations did not change with the tilting angle. The electron concentration (in a single energy valley) obtained from the analysis of the period of the SdH oscillations ($n_{SdH} = 8 \times 10^{17}$ cm$^{-3}$) perfectly corresponds to the total concentration obtained from the low-field Hall effect.
(n_H = 3.2 \times 10^{18} \text{ cm}^{-3})$. The factor of 4 difference is due to the L valley 4-fold degeneracy in Pb_{1-x}Sn_xSe. Since the bulk contribution dominates the total conductivity at low temperatures, the SdH oscillations due to topological surface states are not visible in our crystals. The very small contribution of surface states to the conductivity at low temperatures is typically observed in other well established topological insulators [22-25].

**Supplementary Figure 6.**

**High-field magnetotransport measurements.** The high-field longitudinal resistivity $\rho_{xx}$ (a) and transverse resistivity $\rho_{xy}$ (b) of the Pb_{0.77}Sn_{0.23}Se sample at several temperatures. Fig. 6c presents the $\rho_{xy}$ data after subtraction of the linear term.

**Supplementary Figure 7.**

**Shubnikov-de Haas oscillations.** The high-field magnetoresistance data recorded for a Pb_{0.77}Sn_{0.23}Se sample at the temperature $T = 4.2$ K in tilted magnetic fields. The tilting angle $\beta$ is the angle between the external magnetic field and the normal of the (001) sample plane.
S5 Tight-binding (TBA) calculations: the crystal-slab-thickness dependence.

In the case of the critical Sn composition \( x_c = 0.381 \) the calculated fundamental bulk bandgap at the L-point of the Brillouin zone is closed. However, in our calculations performed for crystal slabs of finite thickness we observe a small gap at the \( \bar{X} \)-point. This effect is due to the electron confinement as verified by the calculation of the bandgap dependence on the crystal-slab thickness. We have calculated the bandgaps at various points of the surface Brillouin zone for \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) crystal slabs of varying thickness up to about 160 nm. Supplementary Fig. 8 presents the results in two cases. For the fundamental gap at the \( \bar{X} \)-point in the crystal with critical Sn content \( x = x_c \) the finite-size effect is clearly observed. The bandgap is inversely proportional to the slab thickness (blue line), as expected, and decreases asymptotically to zero with increasing slab thickness. In contrast, the surface states bandgap in the \( \bar{X} - \bar{M} \) direction in the crystal with a Sn content \( x = 0.6 \) (red line) remains constant for thick slabs thus proving its intrinsic origin. In this case the gap is not determined by the electron confinement. Its apparent dependence on the thickness for very thin slabs stems from the surface wave functions overlap.

**Supplementary Figure 8.**
TBA calculations of the crystal-slab-thickness dependence of energy gaps in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \). The blue line shows the bandgap at the \( \bar{X} \)-point in \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) with a Sn content \( x = x_c = 0.381 \), whereas the red line displays the bandgap on the \( \bar{X} - \bar{M} \) line for a Sn content \( x = 0.6 \). For the Sn content range investigated, the thickness of one monolayer is about 3.2 Å.