IRis

Northeastern University

Physics Faculty Publications

Department of Physics

January 01, 2010

A new platform for topological quantum phenomena : topological Insulator states in thermoelectric Heusler-related ternary compounds

H. Lin
Princeton University

L. A. Wray
Princeton University

Y. Xia
Princeton University

S. Jia
Princeton University

R. J. Cava
Princeton University

See next page for additional authors

Recommended Citation

Lin, H.; Wray, L. A.; Xia, Y.; Jia, S.; Cava, R. J.; Bansil, A.; and Hasan, M. Z., "A new platform for topological quantum phenomena : topological Insulator states in thermoelectric Heusler-related ternary compounds" (2010). *Physics Faculty Publications*. Paper 8.
http://hdl.handle.net/2047/d20000361

This work is available open access, hosted by Northeastern University.

Author(s)
H. Lin, L. A. Wray, Y. Xia, S. Jia, R. J. Cava, A. Bansil, and M. Z. Hasan

This text is available at IRis: http://iris.lib.neu.edu/physics_fac_pubs/8

A new platform for topological quantum phenomena: Topological Insulator states in thermoelectric Heusler-related ternary compounds

H. Lin,[1,2] L.A. Wray,[1] Y. Xia,[1] S. Jia,[3] R.J. Cava,[3] A. Bansil,[2] and M.Z. Hasan[1,4,5]

[1] *Joseph Henry Laboratories of Physics, Princeton University, Princeton, New Jersey 08544, USA*
[2] *Department of Physics, Northeastern University, Boston, Massachusetts 02115, USA*
[3] *Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA,*
[4] *Princeton Center for Complex Materials, Princeton University, Princeton, New Jersey 08544, USA*
[5] *Princeton Institute for Science and Technology of Advanced Materials. PRISM, Princeton University, Princeton, New Jersey 08544, USA**

(Dated: February 28, 2010)

Topological insulators realize a novel state of quantum matter that are distinguished by topological invariants of bulk band structure rather than spontaneously broken symmetries. A number of exotic quantum phenomena have been predicted to exist in multiply-connected geometries which require an enormous amount of materials flexibility. We have extended our previous search for TI materials from binary (Bi_2X_3 series, Xia *et.al.*, Nature Phys. **5**, 398 (2009)) to the thermoelectric ternary compounds. We discover that the distorted LuPtSb is the first ternary compound of the "$MM'X$" series harboring a 3D topological insulator state with Z_2=-1 whereas TiNiSn is trivial. We also show that the half-Heusler LuPtSb-type series is a natural platform that hosts a range of candidate compounds, alloys and artificial heterostructures (quantum-wells). We also discovered several different paradigms of trivial and non-trivial topological ordering in this class, including an intrinsically metallic nontrivial topological state in YAuPb. Some of these materials are grown (results will be reported separately).

PACS numbers:

arXiv:1003.0155v1 [cond-mat.mes-hall] 28 Feb 2010

Topological insulators (TI)[1–7] realize a novel state of quantum matter that are distinguished by topological invariants of bulk band structure rather than spontaneously broken symmetries. Its material realization in 2D artificial HgTe-quantum wells [2, 6] and 3D Bi-based binary compounds [3, 7–16] led to a surge of interest in discovering novel topological physics in world-wide condensed matter community. A number of exotic quantum phenomena have been predicted to exist in multiply-connected geometries [17–23] which require an enormous amount of materials flexibility. Given the right materials, these topological properties naturally open a window to new realms of spintronics and quantum computing. Just as the majority of normal metals are neither good superconductors nor strongly magnetic, there is no inherent likelihood that the band structure of topological insulators known so far will be suitable for the realization of any of the novel physical states or devices that have been predicted for quantum computing or spintronics. We need to expand our search. We have extended our previous search for TI materials from binary (Bi_2X_3 series, Xia *et.al.*, Nature Phys. **5**, 398 (2009)) to the thermoelectric ternary compounds. We discover that the distorted LuPtSb is the first ternary compound of the "$MM'X$" series harboring a 3D topological insulator state with Z_2=-1. We also show that the half-Heusler LuPtSb-type series is a natural platform that hosts a range of candidate compounds, alloys and artificial heterostructures (quantum-wells). We also discovered several different paradigms of trivial and non-trivial topological ordering in this class, including an intrinsically metallic nontrivial topological state in YAuPb. In this Letter, we use first principles theoretical calculations to show that distorted LuPtSb is the first ternary compound expected to realize a three dimensional topological insulator state.

The crystal lattice of half-Heusler ternary compounds is described by the space group $F\bar{4}3m$, with the atomic arrangement shown in Fig. 4a. Crystalline compounds of this structure are very common, and are customarily assigned the chemical formula "$MM'X$", where M, M', and X atoms occupy the Wyckoff 4b, 4c, and 4a positions respectively [28]. The M' and X atoms form a zincblende lattice, when taken alone. Atoms of M fill empty space within the zincblende structure and form NaCl-like ionic pairs together with X atoms. These materials closely resemble the previously known topologically nontrivial compound HgTe [2, 6], which achieves topological order with a zincblende structure, and can be considered to belong to the class of half-Heusler TIs if one assigns a vacancy to the M site (M= void, denoted by []) and sets M'=Hg and X=Te. There is no spatial inversion symmetry in zincblende and half-Heusler structures.

$Hg_{1-x}Cd_xTe$ is a family of strong spin orbit 3D materials (Dornhaus and Numtz, 1983)[24]. In the electronic structure of CdTe the conduction band edge states have an s like symmetry, while the valence band edge states have a p like symmetry. In HgTe, the p levels rise above the s levels, leading to an inverted band structure. Due to this similarity, it is instructive to begin our discussion of half-Heusler band structure topology by examining the

*Electronic address: mzhasan@princeton.edu

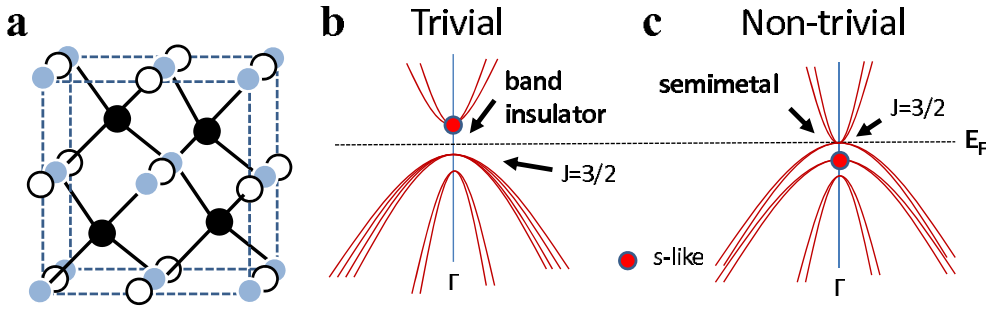

FIG. 1: **Half-Heusler crystal structure and band inversion**: **a** The crystal structure of half-Heusler compounds $MM'X$. M, M', and X is denoted by open, black, and gray circles. The zincblende structure formed by M' and X is emphasized by black lines. Diagrams in **b-c** illustrate band structures near the Γ-point for trivial and non-trivial cases, respectively. Red dots denote the s-like orbitals at Γ-point. Band inversion occurs in the non-trival case where the s-like orbitals at the Γ-point are below the four-fold degenerate $j = 3/2$ bands.

nontrivial topological nature of well studied 3D-HgTe. While the related material, CdTe (half-Heusler []CdTe) is a typical band insulator, HgTe is topologically nontrivial due to the inversion of two groups of bands with respective s- and p- orbital symmetry at the Γ-point. The different ordering of band symmetries at the Γ-point for trivial and non-trivial cases are summarized in Fig. 4b-c, with red dots labeling the bands with large s-orbital occupancy. In the trivial case, the s-like orbital is above the band gap, and in the nontrivial case, the s-like orbital at the Γ-point is below the four-fold degenerate $j = 3/2$ bands [2][3]. This band inversion only occurs near the Γ-point and is absent at other special time reversal invariant points. We will show that ternary half-Heusler compounds also exhibit these two topologically distinct classes, distinguished in the same way through orbital symmetries on the X-sublattice.

The calculated (DFT-GGA) band structures of three characteristic half-Heusler materials, LuPtSb, YAuPb, and TiNiSn along high symmetry lines in the Brillouin zone are presented in Fig. 5. A common feature of these materials is that the top of the valence band is located at the Γ-point. Away from Γ, the Fermi level is completely gapped with the exception of electron pockets found at the X-point in YAuPb, where a direct gap is still present between the conduction and valence bands. Therefore, the topological properties can be determined from observations of band structure only near the Γ-point. Other materials with similar properties are addressed in the supplementary information.

Confining our view to band structure very close to the Fermi level (Fig. 5a(inset)), we find that the orbital angular momentum symmetries of these ternary half-Heusler compounds are identical to those defining low energy properties in HgTe and CdTe. For LuPtSb, two upward-concave bands and two downward-concave bands are degenerate at the Γ point. The Fermi energy should lie exactly at this degenerate point for undoped samples. These four-fold degenerate states at the Γ-point have p-type orbital symmetry with a total angular momentum eigenvalue of $j = 3/2$, and lie above a two-fold degenerate s-like state, representing an inversion relative to the natural order of s- and p-type orbital derived band structure. Away from the Γ-point, the upward dispersing bands gain significant s-like character due to orbital hybridization. The same band inversion also occurs in YAuPb, but low energy properties in YAuPb are complicated by another set of conduction bands that comes below the Fermi energy to form electron pockets near X. Thus, by analogy with HgTe, we expect YAuPb to be a topologically nontrivial metal (or "topological metal"), as is the case with elemental antimony [9], and its conductivity could probably be manipulated through alloying, just as antimony was alloyed with bismuth to discover the first known example of a three dimensional TI [7] ($Bi_{1-x}Sb_x$). The s-type bands in TiNiSn are above E_F and very high in energy (not shown), above the $j = 3/2$ bands, meaning that its band structure lacks the s/p inversion that leads to strong topological order. As we will establish more rigorously below, these symmetries correctly indicate that TiNiSn is topologically trivial while LuPtSb and YAuPb are topologically nontrivial.

In terms of the symmetry notation that has been applied to HgTe in previous literature, our calculations show that bands near E_F at the Γ-point possess Γ_6 (2-fold degenerate), Γ_7 (2-fold degenerate), and Γ_8 (4-fold degenerate) symmetry in all of these compounds. Both LuPtSb and HgTe have Γ_8 states at E_F. The Γ_6 symmetry bands are below Γ_8 and occupied, providing the band inversion that distinguishes topological order. Although the order of Γ_7 and Γ_6 is different, it is not relevant to the topological nature since both are occupied. In the band structures of topologically trivial band insulators TiNiSn and CdTe, the Γ_6 states are above the downward dispersing valence bands. These non-inverted Γ_6 states lie above E_F and are unoccupied. It is due to the occupancy of Γ_6 bands at the Γ-point in LuPtSb that the Z_2 topological invariant picks up an extra factor of -1 when compared to TiNiSn.

Therefore, the half-Heusler ternary compound YPtSb with expanded (over LuPtSb) lattice constants is proven to be a topological semimetal, sharing a common Z_2

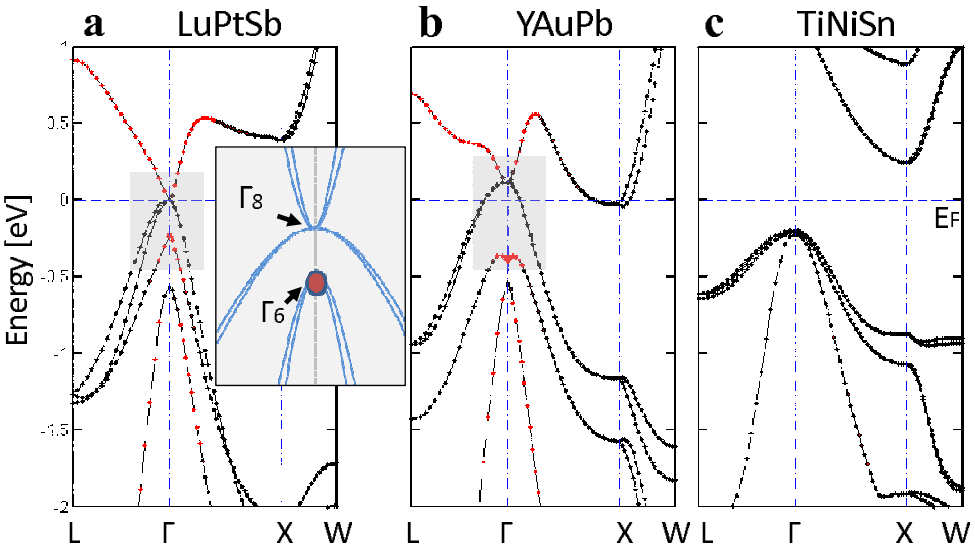

FIG. 2: **Half-Heusler band structures**: Bulk band structures of (**a**) LuPtSb, (**b**) YAuPb, and (**c**) TiNiSn. The size of red data points is proportional to the probability of s-orbital occupation on the anion atom ("X"). An inset in panel **a** highlights inverted band symmetries associated with topological order, corresponding to the the diagram in Fig. 1c.

topological invariant with TIs. When we replace Y by Lu to get LuPtSb the low energy band topology is unchanged, because Y^{+3} and Lu^{+3} are both first column transition metals differing by the presence of $5s^2 4d^{10} 5p^6 4f^{14}$ filled shells. The additional occupied states are complete shells and the Z_2 invariant cannot change. Finally, we continuously shrink the lattice until the experimental lattice constants of LuPtSb are reached. In the whole process, the Γ_6/Γ_8 band inversion at the Γ-point persists and the low energy Hamiltonian undergoes an adiabatic transformation without phase transition. Therefore, we have proven that LuPtSb belongs to the nontrivial Z_2=-1 class.

The fact that none of the topologically nontrivial materials discussed in this work (3D-HgTe, LuPtSb, YAuPb) are naturally insulating known to be due to the Γ-point degeneracy of positive- and negative-mass bands with Γ_8 symmetry, which results from the crystal symmetry group. Distortion of the crystal lattice through static pressure or finite size effects can lift the degeneracy and open a gap at E_F, causing a direct gap between the topologically inverted valence and conduction bands and resulting in the appearance of topologically defined surface states. Fu and Kane have previously discussed this possibility for 3D-HgTe[3]. In Fig. 5b, we demonstrate that a perturbative rhombohedral lattice distortion caused by uniaxial pressure will lift the band structure degeneracy in LuPtSb, resulting in a fully gapped topological insulator state. With reference to the standard axial labeling convention for half-Heusler compounds, a 3% compression is applied along the [111] direction and a 3% expansion in the plane perpendicular to [111]. As has been observed when distortion is applied to the zincblende structured binary compound HgTe, bulk band structure of the distorted half-Heusler LuPtSb is fully gapped and realizes strong Z_2 topological order.

Conversely, the topological band inversion in LuPtSb can be removed altogether by uniformly decreasing all lattice constants, demonstrating the sensitive chemical tunability in this TI class (Fig. 5c). After a 3% reduction in all lattice parameters, the s-like Γ_6 symmetry bands are observed to rise above the Γ_8 bands, removing band inversion at the Γ-point and resulting in a topologically trivial band insulator state.

In conclusion, we have discovered a new class of topological insulator materials realized by distorted half-Heusler compounds, and demonstrated band structure topology calculations for representative topologically non-trivial semimetal (LuPtSb) and nontrivial metallic (YAuPb) undistorted materials. Bulk band structure in LuPtSb is shown to be characterized by Z_2=-1. A large number of topological compounds exist (list to be discussed elsewhere) in this ternary material class, making it a versatile platform for exploring many different device configurations for realizing topological quantum phenomena not accessible in the binary topological insulator classes such as the Bi_2Se_3 series discovered previously.

M.Z.H. acknowledges discussions with C.L. Kane and B.A. Bernevig and support from U.S.DOE and A.P. Sloan Research Fellowship. H.L. acknowledges support from Northeastern and Princeton University. R.J.C. acknowledges discussions and long-standing collaborations with C. Felser and T. Kilmczuk on thermoelectric and superconducting-Heusler phases and with Y.S. Hor on Ternary-topological-materials.

Methods summary: First-principles band calculations were performed with the linear augmented-plane-wave (LAPW) method using the WIEN2K package [29]

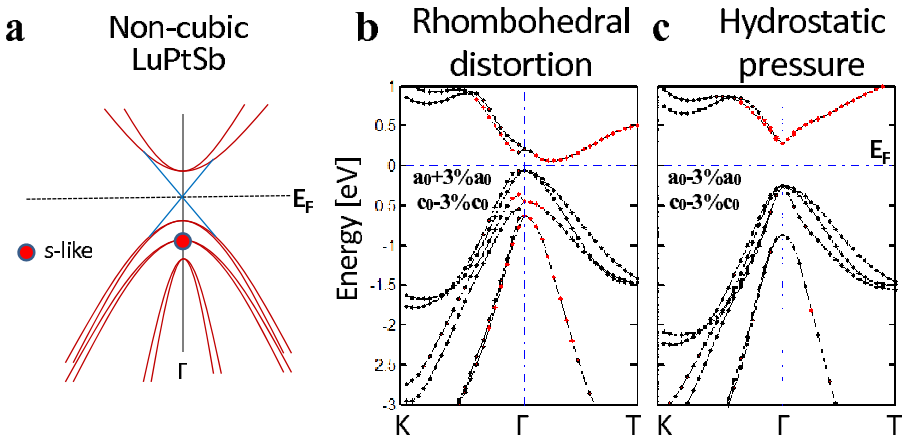

FIG. 3: **The topological insulator state with a single-Dirac-cone**: (a) A sketch of band structure near the Γ-point for topologically non-trivial LuPtSb with a lattice distortion. The s-like Γ_6 states are marked with a red dot. Lattice distortion causes a gap to open at E_F, resulting in a topological insulator state. For such a topological insulator, the surface bands will span the bulk band gap and should have an odd number of Dirac cones, resembling the dispersion plotted with blue lines. (b) Band structures of rhombohedral distorted LuPtSb with lattice constants $a = a_0 + 3\% a_0$ and $c = c_0 - 3\% c_0$ where a_0 and c_0 correspond to the experimental lattice. (c) Band structures of LuPtSb under hydrostatic pressure where $a = a_0 - 3\% a_0$ and $c = c_0 - 3\% c_0$.

in the framework of density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [30] was used to describe the exchange-correlation potential. Spin orbital coupling (SOC) was included as a second variational step using a basis of scalar-relativistic eigenfunctions.

[1] Kane, C. L. & Mele, E. J. Z_2 Topological Order and the Quantum Spin Hall Effect. *Phys. Rev. Lett.* **95**, 146802 (2005).

[2] Bernevig B. A., Hughes T. L., Zhang S.-C. Quantum spin Hall effect and topological phase transition in HgTe quantum wells. *Science* **314**, 1757 (2006).

[3] Fu, L. and C.L. Kane Topological Insulators with Inversion Symmetry (including 3D-HgTe and Bi-Sb). Phys. Rev. B **76**, 045302 (2007).

[4] Fu, L., Kane, C. L., & Mele, E. J. Topological insulators in three dimensions. *Phys. Rev. Lett.* **98**, 106803 (2007).

[5] Moore, J. E. & Balents, L. Topological invariants of time-reversal-invariant band structures. *Phys. Rev. B* **75**, 121306(R) (2007).

[6] Konig, M. *et al.* Quantum spin Hall insulator state in HgTe quantum wells. *Science* **318**, 766 (2007).

[7] Hsieh, D. *et al.* A topological Dirac insulator in a quantum spin Hall phase. *Nature (London)* **452**, 970 (2008).

[8] Hsieh, D. *et al.* A tunable topological insulator in the spin helical Dirac transport regime. *Nature (London)* **460**, 1101 (2009).

[9] Hsieh, D. *et al.* Observation of unconventional quantum spin textures in topological tnsulators. *Science* **323**, 919 (2009).

[10] Xia, Y. *et al.* Observation of a large-gap topological-insulator class (Bi_2Se_3 class) with a single Dirac cone on the surface. *Nature Phys.* **5**, 398 (2009). http://dx.doi.org/10.1038/nphys1294 http://dx.doi.org/10.1038/nphys1274

[11] Noh, H.-J. *et al.*, Spin-orbit interaction effect in the electronic structure of Bi_2Te_3 observed by angle-resolved photoemission spectroscopy, *Europhys. Lett.* **81**, 57006 (2008).

[12] Roushan, P. *et al.* Topological surface states protected by chiral spin textures *Nature (London)* **460**, 1106 (2009).

[13] Zhang, H. *et al.* Topological insulators in Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 with a single Dirac cone on the surface. *Nature Phys.* **5**, 438 (2009).

[14] Chen, Y.L. *et al.*, Realization of a Three Dimensional Topological Insulator Bi_2Te_3, Science **325**, 178 (2009).

[15] Hsieh, D. *et al.* Observation of time-reversal-protected single-Dirac-cone spin-polarized topological-insulator states in Bi_2Te_3 and Sb_2Te_3. *Phys. Rev. Lett.* **103**, 146401 (2009).

[16] Wray, L.A. *et al.* Observation of unconventional band topology in a superconducting doped topological insulator Cu_x-Bi_2Se_3.Preprint at ⟨http://arxiv.org/abs/0912.3341⟩ (2009).

[17] Fu, L. and C.L. Kane Superconducting proximity effect and Majorana fermions at the surface of a topological insulator, Phys. Rev.Lett. **100**, 096407 (2008).

[18] Fu, L. & Kane, C. L. Probing neutral Majorana fermion edge modes with charge transport. *Phys. Rev. Lett.* **102**, 216403 (2009).

[19] Qi X.-L. *et al.* Inducing a magnetic monopole with topological surface states. *Science* **323**, 1184 (2009)

[20] Teo, J. C.Y. & Kane, C. L. Majorana fermions and non-Abelian statistics in three dimensions. Phys. Rev. Lett. **104**, 046401 (2010).

[21] Lee, D.-H. Surface States of Topological Insulators: The

Dirac Fermion in Curved Two-Dimensional Spaces. *Phys. Rev. Lett.* **103**, 196804(2009).

[22] Law, K. P.A. Lee, T. Ng, Majorana Fermion Induced Resonant Andreev Reflection. *Phys. Rev. Lett.* **103**, 237001 (2009).

[23] Xu, C. Quantum critical points of helical Fermi liquids. *Physical Review B* **81** 054403 (2010).

[24] Dornhaus R. and G. Nimtz, 1983, Narrow Gap Semiconductors, Springer Tracts in Modern Physics 98 (Springer, Berlin).

[25] Tobola J. and J. Pierre, Electronic phase diagram of the XTZ semi-Heusler compounds, *J. Alloys Compd. (Switzerland)* **243**, 296 (2000).

[26] Mastronardi,K., D. Young, C.-C. Wang, A.P. Ramirez, P. Khalifah, and R.J. Cava, Antimonides with the Half-Heusler Structure: New Thermoelectric Materials *Appl. Phys. Lett.* **74**, 1415 (1999).

[27] Kandpal, H.C., C. Felser and R. Seshadri Covalent bonding and the nature of band gaps in some half-Heusler compounds, *J. Phys. D: Appl. Phys.* **39**, 776785 (2006).

[28] Wyckoff, R. W. G. Crystal Structures (Krieger, Melbourne, FL, 1986), Vol. 2.

[29] Blaha, P., K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, (Karlheinz Schwarz, Techn. University Wien, Austria), 2001.ISBN 3-9501031-1-2.

[30] Perdew, P. et al., *Phys. Rev. Lett.* **77**, 3865 (1996).

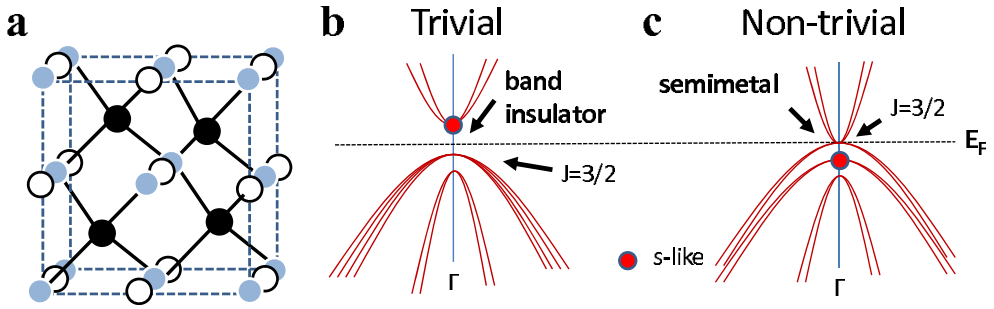

FIG. 4: **Half-Heusler crystal structure and band inversion**: **a** The crystal structure of half-Heusler compounds $MM'X$. M, M', and X is denoted by open, black, and gray circles. The zincblende structure formed by M' and X is emphasized by black lines. Diagrams in **b-c** illustrate band structures near the Γ-point for trivial and non-trivial cases, respectively. Red dots denote the s-like orbitals at Γ-point. Band inversion occurs in the non-trival case where the s-like orbitals at the Γ-point are below the four-fold degenerate $j = 3/2$ bands.

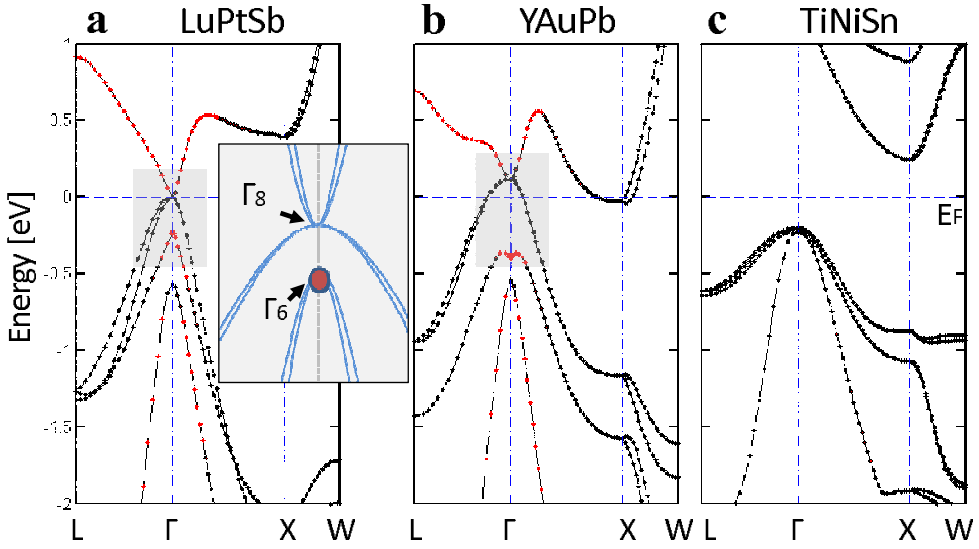

FIG. 5: **Half-Heusler band structures**: Bulk band structures of (**a**) LuPtSb, (**b**) YAuPb, and (**c**) TiNiSn. The size of red data points is proportional to the probability of s-orbital occupation on the anion atom ("X"). An inset in panel **a** highlights inverted band symmetries associated with topological order, corresponding to the the diagram in Fig. 1c.

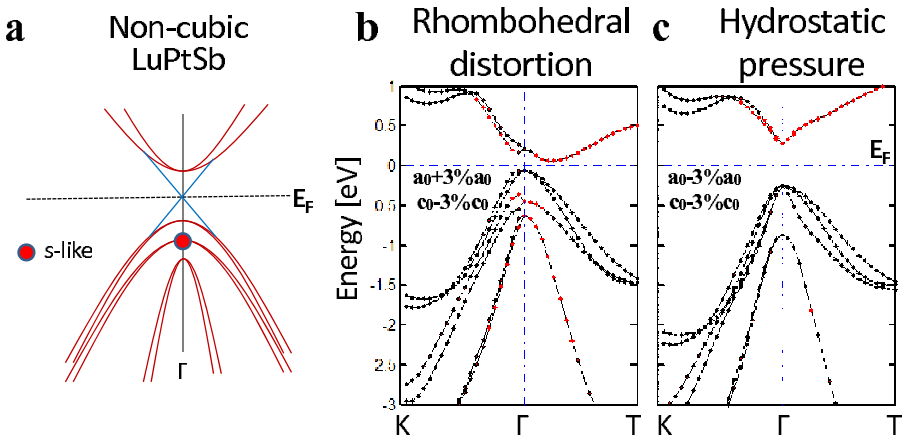

FIG. 6: **The topological insulator state with a single-Dirac-cone**: (a) A sketch of band structure near the Γ-point for topologically non-trivial LuPtSb with a lattice distortion. The s-like Γ_6 states are marked with a red dot. Lattice distortion causes a gap to open at E_F, resulting in a topological insulator state. For such a topological insulator, the surface bands will span the bulk band gap and should have an odd number of Dirac cones, resembling the dispersion plotted with blue lines. (b) Band structures of rhombohedral distorted LuPtSb with lattice constants $a = a_0 + 3\% a_0$ and $c = c_0 - 3\% c_0$ where a_0 and c_0 correspond to the experimental lattice. (c) Band structures of LuPtSb under hydrostatic pressure where $a = a_0 - 3\% a_0$ and $c = c_0 - 3\% c_0$.