Ultrathin Films of Superconducting Metals as a Platform for Topological Superconductivity

Chao Lei, Hua Chen, and Allan H. MacDonald

Phys. Rev. Lett. **121**, 227701 — Published 29 November 2018

DOI: 10.1103/PhysRevLett.121.227701

Ultrathin Films of Superconducting Metals as a Platform for Topological Superconductivity

Chao Lei,[1] Hua Chen,[2,3] and Allan H. MacDonald[1]

[1]*Department of Physics, The University of Texas at Austin, Austin, Texas 78712,USA*[*]
[2]*Department of Physics, Colorado State University, Fort Collins, CO 80523, USA*
[3]*School of Advanced Materials Discovery, Colorado State University, Fort Collins, CO 80523, USA*

The ingredients normally required to achieve topological superconductivity (TSC) are Cooper pairing, broken inversion symmetry, and broken time-reversal symmetry. We present a theoretical exploration of the possibility of using ultra-thin films of superconducting metals as a platform for TSC. Because they necessarily break inversion symmetry when prepared on a substrate and have intrinsic Cooper pairing, they can be TSCs when time-reversal symmetry is broken by an external magnetic field. Using microscopic density functional theory calculations we show that for ultrathin Pb and β-Sn superconductors the position of the Fermi level can be tuned to quasi-2D band extrema energies using strain, and that the g-factors of states at time-reversal invariant momentum can be extremely large, enhancing the influence of external magnetic fields.

Introduction—Topological superconductors (TSC)[1–6] can host fault-tolerant qubit operations based on the exchange properties[7, 8] of Majorana zero modes located either at the ends of topological superconducting quantum wires[9], or in the vortex cores of two-dimensional TSCs[1, 3, 7, 10]. For weak Cooper pairing, topological superconductivity occurs whenever the host normal metal has an odd number of closed Fermi surfaces. Class D type TSC was achieved some time ago[11–14] by combining [15–17] low density-of-states semiconductors, strong spin-orbit coupling and external magnetic fields that lift band spin-degeneracies, and Cooper pairing provided by an adjacent superconductor. In recent research semiconductor-based TSCs have been further refined[18, 19], and other possibilities have also been realized experimentally, including the TSCs based on magnetic atomic chains on superconducting substrates[20–22] and two-dimensional (2D) TSCs based on topological insulator surface states[23, 24].

TSC has been proposed as a theoretical possibility in bulk superconductors that might have chiral order parameters [25–32], for example in noncentrosymmetric superconductors[28, 29, 32] with broken time-reversal or inversion symmetry. These intrinsic systems, including $SrTiO_3/LaAlO_3$ heterostructures [25, 27, 33, 34], bulk Sr_2RuO_4, and superfluid He^3, have some potential advantages over the artificial hybrid materials systems in which TSC has already been achieved experimentally. There is however no intrinsic system in which all the ingredients required for TSC states are fully established. The case of class D TSC based on s-wave pairing in $SrTiO_3/LaAlO_3$ two-dimensional electron gases, for example[33, 34], requires Zeeman splitting larger than pair potential and this is difficult to achieve without destroying superconductivity given this system's relatively small g-factors[35]. Other proposals [25–32] hold promise, but require further research to confirm the exotic pair potentials on which they are based.

In this article we propose a different possibility, namely establishing 2D TSC directly in ultrathin films of superconducting metals [36], instead of semiconductors, thereby avoiding problems associated with establishing proximity coupling between a semiconductor and a superconductor. We are motivated by recent experimental demonstrations of strong robust superconductivity in ultra-thin metal films [37–39], and by proposals for realizing topological superconductivity based on strong Rashba-like spin-orbit interactions in the surface-states of heavy metals TSC[40, 41]. We show that quasi 2D band extrema in ultra-thin superconducting films can occur close to the Fermi level, that in the cases of Pb and β-Sn films the g-factors at the relevant band edges can be extremely large, and that band positions can be tuned by strain. We predict that these ingredients will allow thin superconducting films to be tuned to TSC states when time-reversal invariance is broken by a weak magnetic field or a proximitized exchange interaction[39].

We concentrate below on lead (Pb) and β-Sn thin films. Using *ab initio* density functional theory (DFT) calculations [42], we show that the strength of inversion symmetry breaking in β-Sn and Pb thin films can be controlled by varying either film thickness or substrate material, that Fermi level positions relative to band extrema are more easily tuned by strain than by gate electric fields, and that typical g-factors[43] at band extrema are extremely large. Strains can be varied experimentally by placing the thin film on a piezoelectric substrate as illustrated in Fig. 1, and adjusted to tune in topologically non-trivial states.

Superconducting metal thin film as TSCs — For weak pairing TSC occurs in bands that are effectively spinless when an odd number of them cross the Fermi energy. In quasi-2D systems with strongly broken inversion symmetry, Rashba-like spin-orbit interactions lift spin-degeneracies except at the time-reversal invariant $\boldsymbol{k}$ points where Kramers theorem applies. The Kramers degeneracy can be lifted only by breaking time-reversal invariance, for example by an external magnetic field. A

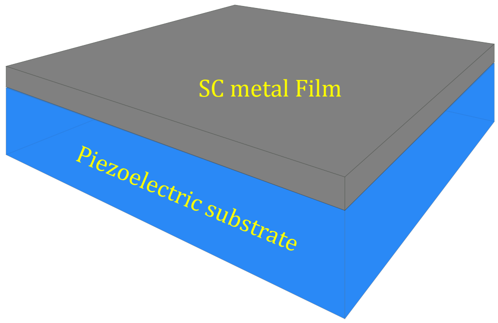
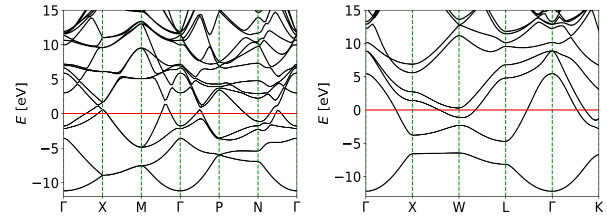


FIG. 1: Schematic illustration of an ultra-thin heavy superconducting(SC) metal film grown on a piezoelectric substrate. An electric field applied to the substrate can then be used to tune the film into a topological superconducting state.



(a) Bandstructure of β-Sn (b) Bandstructure of Pb

FIG. 2: Bandstructure of bulk β-Sn and Pb. The red horizontal lines mark the Fermi level. These bands are consistent with literature results for β-Sn [52, 53] and Pb [54]. Thin film quasi-2D bands can be crudely estimated from these bulk bands by discretizing the surface-normal momentum component.

minimal mean field theory shows that, like the current semiconductor systems, these TSCs are class D according to the Altland-Zirnbauer (AZ) classification [42, 44] which is also the main class of systems (1D or 2D) studied in present experiments. For sufficiently strong spin-orbit coupling a class D TSC state is realized when $\Delta_z = g\mu_B B > \sqrt{\Delta^2 + \mu^2}$, where Δ_z is the Zeeman energy, Δ is the pair potential, and μ is the chemical potential measured from the zero-field band energy at the time-reversal invariant $\boldsymbol{k}$-point. Topological superconductivity in quasi-2D systems therefore requires that μ be small and that the g-factor that describes the Kramers degeneracy splitting be large. A quasi-2D metal film has the advantage over its bulk counterpart that it has a greater density of bands, which increases the chances for large g-factors and is essential, as we shall see, if we want to find materials with small value of μ. Comparing the criteria that support large g-factors [45, 46] with patterns in the occurrence of superconductivity[47] suggests ultra-thin films of β-Sn and Pb as promising candidates for topological superconductivity.

TABLE I: Calculated g-factors at the Γ point for the band closest to the Fermi level in bulk and in thin films of β-Sn and Pb on a As_2O_3 substrate.[42, 43] For the films the average values of the g-factors of 12 subbands around fermi level is also given. The g-factors are obtained by evaluating the splitting between a Kramers pair at the Γ point under a magnetic field. For the thin films the magnetic field is along the film normals [(111) for Pb and (001) for β-Sn], while for bulk Pb and β-Sn it is along the z-axis [(001) direction].

β-Sn	g-factor	avg.	Pb	g-factor	avg.
bulk	681		bulk	132	
7 layers	29	254	5 layers	57	140
9 layers	572	243	7 layers	161	73
11 layers	574	268	9 layers	198	186

Pb has a face-centered-cubic structure [42] and is a widely studied superconductor with a bulk T_c= 7.19 K. Among the several stable phases of bulk Sn only β-Sn, which has a tetragonal structure (A5)[42], is a superconductor[48] with $T_c = 3.72$ K. The bands of β-Sn and Pb, illustrated in Fig. 2, reflect strong $s - p$ hybridization. Bulk β-Sn and bulk Pb both have inversion symmetry, and therefore even degeneracies of all bands throughout the Brillouin zone.

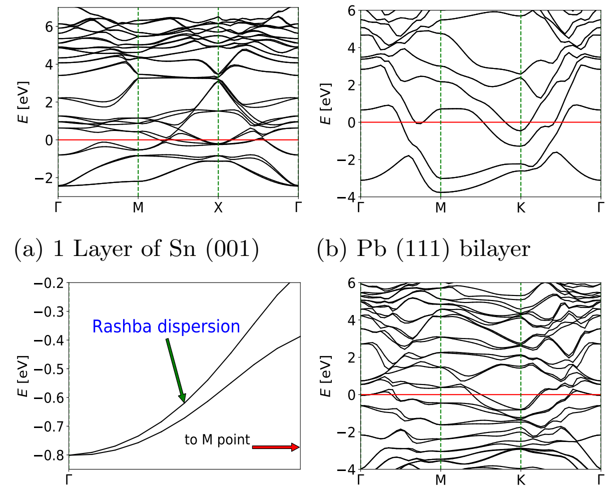
We evaluated g-factors using methods informed by recent advances in the *ab initio* description of orbital magnetism [43, 49–51]. According to our calculations[43], the Γ point g-factors of bulk β-Sn and bulk Pb are very large, as summarized in Table I. In Fig. 2 we see that a strongly dispersive band crosses the Fermi energy along Γ-X in β-Sn and along Γ-L in Pb. Based on this observation, we expect that quasi-2D subband extrema at energies close to the Fermi energy will occur at 2D Γ points in thin films with surface normals along the (111) direction and the (001) direction for Pb and β-Sn respectively. Indeed, it is (111) growth direction Pb films that are commonly studied experimentally. [37].

In thin films the inversion symmetry of a bulk structure does not survive for all surface terminations and thicknesses, even when the film structure consists of bulk unit cells repeated in the film normal direction. For β-Sn films grown along the (001) direction, inversion symmetry is absent when the number of atomic layers is odd[55]. As an illustration, the band structure of single layer Sn (001) is shown in Fig. 3a. The band closest to the Fermi level, which has its extremum near Γ, exhibits typical Rashba spin-orbit coupling behavior as illustrated in Fig. 3c. Similar quasi-2D bands are present for all odd-layer-number β-Sn (001) thin films[42]. The Rashba spin-orbit coupling strength becomes smaller with increasing number of layers. However, even at 15 layers, its value is still about 0.85 eV Å, which is several times larger than that in semiconductor quantum wires ($\sim$0.2 eV Å[13]).

For Pb (111), on the other hand, inversion symmetry is maintained at all film thicknesses and every subband has two-fold degeneracy throughout the 2D Brillouin zone. Fig. 3b shows the example of a two-layer Pb (111) thin film (see [42] for more band structures for different number of layers). Broken inversion symmetry must then come from hybridization with a substrate. In the calculations described below we have used a single quintuple layer of As_2O_3 with the Bi_2Te_3 structure as the substrate because it is insulating and, according to our DFT calculations, lattice-matched to Pb (111). The resulting quasi-2D band structure is illustrated in Fig. 3d (results for other thicknesses can be found in [42]). We can see in the figure that the extremum of the lowest band at Γ exhibits Rashba spin splitting. The Rashba spin-orbit coupling of Pb thin films on As_2O_3 is 0.15-0.4 eVÅon average (0.01, 0.2, 0.34, and 0.05 eVÅrespectively for the four subbands around Fermi level [42]), which is much larger than that on Si substrates[56, 57] (0.03-0.04 eV Åfor 10 layers of Pb). The averaged Rashba spin-orbit coupling decreases with increasing film thickness, but even for the thicker films considered here it is still large compared with that in semiconductor quantum wires on s-wave superconductors[13].

We also studied heavier substrates in the Pnictogen Chalcogenides family such as As_2O_3, Sb_2S_3, Sb_2Se_3, Bi_2Se_3, Bi_2Te_3, and found an enhancement of Rashba spin-orbit coupling ranging from 0.3 eVÅ to around 0.7 eVÅ on average [42], and even larger for certain subbands. However, since some of Pnictogen Chalcogenides are topological insulators, those subbands may also be the surface states of topological insulators. For some Pb (111) thicknesses the band extremum closest to the Fermi level lies not at a time-reversal invariant momentum, but at the K-point where spin-splitting is present even in the absence of a magnetic field. In this case, valley symmetry breaking by an external magnetic field is necessary to yield a topological superconducting state.

Tuning the Fermi Level — As illustrated in Figs. 3c and 3d, the scale of the spin-orbit splitting in the metal thin films of interest is a sizable fraction of an eV and comparable to quasi-2D band widths. TSC states will therefore occur whenever the Fermi level is within Δ_z of a band extremum energy. Here Δ_z refers either to spin-splitting at a time-reversal invariant momentum, or to energetic splitting between spin-orbit split states at time-reversal partner momenta. For g-factors $\sim$ 100, these energies are $\sim$ 10 meV at the fields to which superconductivity typically survives. (The Bohr magneton is ~ 0.058meV/T. In Pb (111) thin films, $H_{c\perp} = 1.56$ T for 5 monolayers and 0.63T for 13 monolayers. In-plane critical fields are much larger: $H_{c\|} = 54.9$T for 5 monolayers and 13.6T for 13 monolayers [37]). It follows that TSC states should be realizable if the Fermi level can be tuned to within $\sim$ 10 meV of quasi-2D band extrema, for large Rashba coupling, the most possible pairing of electrons has an intra-band form. Due to the very large



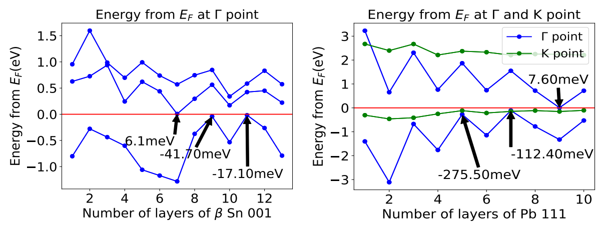
(a) 1 Layer of Sn (001) (b) Pb (111) bilayer

(c) Single layer Sn (001) (d) Pb (111) bilayer

FIG. 3: Band structure of a single layer (3 atomic layers) film of β Sn grown along the (001) direction (a) and a Pb bilayer film grown along the (111) direction (b). (c) Highlight of the first band below the Fermi level in (a) near the Γ-point showing Rashba-like spin-orbit splitting. (d) Pb bilayer grown along the (111) direction on an As_2O_3 substrate exhibiting Rashba-like spin-orbit splitting near the Γ-point.

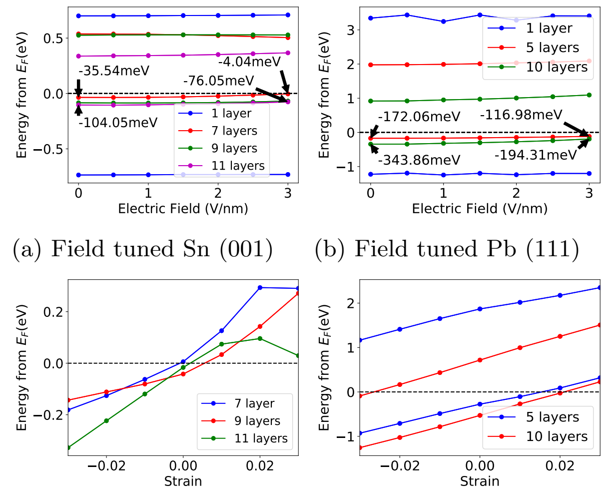
$H_{c\|}$, the system may be driven by in-plane fields into an inter-band pairing phase with finite pairing momentum [58].

Figure 2 shows that bulk β-Sn bands cross the Fermi level along Γ-X, and that bulk Pb bands cross the Fermi level along Γ-L. The bandwidth of β-Sn from Γ to X is about $W = 2.765$eV. It follows that the average distance between quasi-2D subband energies at any particular 2D $\boldsymbol{k}$-point is around $W/2N$, or $\sim$ 150meV for a 10 layer thick film. In Fig. 4a we plot the quasi-2D band energies at the Γ point measured from the Fermi level for odd-layer-number Sn thin films *vs.* the number of layers. As expected the energy separations tend to decrease with increasing film thickness, but are suitably small only occasionally. For the films with thickness of 7, 9 and 11 layers, band extrema are within tens of meV of the Fermi level. The calculated g-factors at the Γ point for these thicknesses are up to around 600. (The g-factors of the films highlighted by arrows in Fig. 4a are presented in Table I.) For bulk Pb the bandwidth from Γ to L is $\sim$ 10 eV, implying larger typical energy separation values. The band separation plot for Pb (111) thin films is presented in Fig. 4b, which shows apparent quantum size effect oscillations due to confinement of electron wave functions along the thickness direction [59]. In spite of the larger typical separations, we find that at some thicknesses band extrema at Γ and K points can be within a few tens of meV of the Fermi level. Since the g-factors we calculated



(a) Energy to E_F [Sn(001)] (b) Energy to E_F [Pb(111)]

FIG. 4: (a) Subband energy extrema measured from E_F in β-Sn thin films grown in (001) direction. Small energy separations are highlighted by numerical values attached to arrows pointing to the position at which they are plotted. The smallest separation is 6.1 meV for a seven layer film. (b) Γ and K-point band extrema relative to the Fermi level for Pb (111) thin films.



(a) Field tuned Sn (001) (b) Field tuned Pb (111)

(c) Strain tuned Sn (001) (d) Strain tuned Pb (111)

FIG. 5: Band extrema tuning via electric field and strain. (a) Γ-point band energy relative to the Fermi level as a function of electric field for a β-Sn (001) thin film. (b)Γ point band energy relative to the Fermi level as a function of electric field for a Pb (111) thin film. (c) Γ point band energy as a function of strain in the $\pm 3\%$ range for β-Sn (001) thin films. (d) Γ point band energy as a function of strain in the $\pm 3\%$ range for Pb (111) thin films.

for Pb thin films, listed in Table I, are as large as ~ 200, topological superconductivity is still a possibility.

Because DFT is not likely to be perfectly predictive, and because energy separations are likely to be influenced by uncontrolled environmental effects, practical searches for TSC in metal thin films will be greatly assisted by *in situ* control. We have examined the efficacy of two possibilities. In Fig. 5a and 5b we show that, in spite of the strong screening effects expected in metals, external electric fields of ~ 1 V/nm in magnitude can still shift subband energy positions by ~ 10 meV for β-Sn (001) and by ~ 20 meV for Pb (111), which might be large enough to tune into topological states in some instances. The field scale of these calculations are however larger than what is typically practical. Assuming linear response a field of 10^{-1}V/nm [60] would typically change level separations by only $\sim$ 1meV. We have therefore also examined strain effects. In Figs. 5c and 5d, energy separations at the Γ point in β-Sn (001) and Pb (111) films are plotted *vs.* strain. The sensitivity of energy separation to a 1% strain is typically more than 50 meV for β-Sn (001) and around ~ 200 meV for Pb (111) (the case with a substrate is similar[42]), suggesting that strains in this range could successfully tune a thin film into a TSC state. Strains of this size can be induced electrically by applying an electric field across a piezoelectric substrate. If strain could be transferred from a substrate with a large piezoelectric effect ($1.6nm/V$)[61], an electric field of 10^{-2} V/nm could give a strain larger than 1%. We conclude that strain is more promising than direct external electric fields for tuning metal thin films into TSC states.

Discussion — Ultra-thin films of strongly spin-orbit-coupled superconducting metals have the advantage, compared to the commonly studied systems composed of semiconductors on superconducting substrates, that no interface or proximity effect is needed to achieve superconductivity in a strongly spin-orbit coupled system. We have shown that superconducting thin films with strong spin-orbit coupling can be driven into a topological superconductor state by tuning with external electric fields or strains. We have evaluated g-factors[43] at the extrema of the quasi-2D bands of Pb and β-Sn, demonstrating that they typically have large values. Large g-factors make it possible to use a magnetic field to tune the superconductor into a topological state without destroying superconductivity and limit the accuracy with which the band extrema energies need to be tuned to the Fermi level.

Ultra-thin film growth[62] is a key challenge that must be met to realize this proposal for topological superconductivity. Metal thin films growth is strongly influenced by quantum-size effects [62] that determine a discrete set of magic thicknesses at which smooth growth is possible. Quantum size effects also imply sensitivity of the two-dimensional subbands and their time-reversal momenta g-factors to layer thickness. However, this should not be a serious probem for materials engineering since thickness can be controlled at the single layer using MBE growth techniques. Once the thin film is grown, the number of layers is fixed. Our g-factor calculations show that in most cases the g-factors at Γ are quite large so that it will be possible to realize TSC if the Fermi level can be tuned close to the edge of a quasi-2D subband. Further restrictions are imposed by the requirement that the film thickness not be too large,[63] otherwise strain tuning can not be effectively employed. Importantly, we expect the topological classification of superconducting states to remain robust in the presence of inevitable disorder, for example disorder due to variations in film thickness. To our best knowledge single crystalline β-Sn thin film growth has not yet been achieved. Recent experiments have however already demonstrated superconductivity with strong spin-orbit coupling[37] in ultrathin films of Pb. Our results motivate experimental efforts to grow the β-Sn thin films and drive β-Sn and Pb thin film into TSC phase with a relatively weak magnetic field, or by depositing magnetic atoms or films.

Acknowledgements.— The authors thank Ken Shih for helpful discussions. This work was supported by the Office of Naval Research under grant ONR-N00014-14-1-0330 and the Welch Foundation under grant TBF1473. The authors acknowledge the Texas Advanced Computing Center (TACC) at The University of Texas at Austin for providing HPC resources that have contributed to the research results reported within this paper.

---

* leichao.ph@gmail.com

[1] C. Beenakker, Annu. Rev. Con. Mat. Phys. **4**, 113 (2013).
[2] C. Beenakker and L. Kouwenhoven, Nat. Phys. **12**, 618 (2016).
[3] A. Stern, Nature **464**, 187 (2010).
[4] A. Jason, Rep. Prog. Phys. **75**, 076501 (2012).
[5] L. Martin and F. Karsten, Semicond. Sci. Technol. **27**, 124003 (2012).
[6] S. Masatoshi and A. Yoichi, Rep. Prog. Phys. **80**, 076501 (2017).
[7] D. A. Ivanov, Phys. Rev. Lett. **86**, 268 (2001).
[8] C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Rev. Mod. Phys. **80**, 1083 (2008).
[9] A. Y. Kitaev, Phys. Usp. **44**, 131 (2001).
[10] N. Read and D. Green, Phys. Rev. B **61**, 10267 (2000).
[11] A. Das, Y. Ronen, Y. Most, Y. Oreg, M. Heiblum, and H. Shtrikman, Nat. Phys. **8**, 887 (2012).
[12] M. T. Deng, C. L. Yu, G. Y. Huang, M. Larsson, P. Caroff, and H. Q. Xu, Nano Lett. **12**, 6414 (2012).
[13] V. Mourik, K. Zuo, S. M. Frolov, S. R. Plissard, E. P. A. M. Bakkers, and L. P. Kouwenhoven, Science **336**, 1003 (2012).
[14] L. P. Rokhinson, X. Liu, and J. K. Furdyna, Nat. Phys. **8**, 795 (2012).
[15] Y. Oreg, G. Refael, and F. von Oppen, Phys. Rev. Lett. **105**, 177002 (2010).
[16] R. M. Lutchyn, J. D. Sau, and S. Das Sarma, Phys. Rev. Lett. **105**, 077001 (2010).
[17] J. D. Sau, R. M. Lutchyn, S. Tewari, and S. Das Sarma, Phys. Rev. Lett. **104**, 040502 (2010).
[18] S. M. Albrecht, A. P. Higginbotham, M. Madsen, F. Kuemmeth, T. S. Jespersen, J. Nygrd, P. Krogstrup, and C. M. Marcus, Nature **531**, 206 (2016).
[19] M. T. Deng, S. Vaitieknas, E. B. Hansen, J. Danon, M. Leijnse, K. Flensberg, J. Nygrd, P. Krogstrup, and C. M. Marcus, Science **354**, 1557 (2016).
[20] S. Nadj-Perge, I. K. Drozdov, J. Li, H. Chen, S. Jeon, J. Seo, A. H. MacDonald, B. A. Bernevig, and A. Yazdani, Science **346**, 602 (2014).
[21] B. E. Feldman, M. T. Randeria, J. Li, S. Jeon, Y. Xie, Z. Wang, I. K. Drozdov, B. Andrei Bernevig, and A. Yazdani, Nat. Phys. **13**, 286 (2016).
[22] R. Pawlak, M. Kisiel, J. Klinovaja, T. Meier, S. Kawai, T. Glatzel, D. Loss, and E. Meyer, npj Quantum Information **2**, 16035 (2016).
[23] Q. L. He, L. Pan, A. L. Stern, E. C. Burks, X. Che, G. Yin, J. Wang, B. Lian, Q. Zhou, E. S. Choi, K. Murata, X. Kou, Z. Chen, T. Nie, Q. Shao, Y. Fan, S.-C. Zhang, K. Liu, J. Xia, and K. L. Wang, Science **357**, 294 (2017).
[24] Y. Zeng, C. Lei, G. Chaudhary, and A. H. MacDonald, Phys. Rev. B **97**, 081102 (2018).
[25] M. S. Scheurer and J. Schmalian, Nature communications **6**, 6005 (2015).
[26] T. Tzen Ong and P. Coleman, Phys. Rev. B **90**, 174506 (2014).
[27] M. S. Scheurer, D. F. Agterberg, and J. Schmalian, npj Quantum Materials **2**, 9 (2017).
[28] M. S. Scheurer, Phys. Rev. B **93**, 174509 (2016).
[29] K. V. Samokhin, Phys. Rev. B **92**, 174517 (2015).
[30] Y. Wang, G. Y. Cho, T. L. Hughes, and E. Fradkin, Phys. Rev. B **93**, 134512 (2016).
[31] F. Loder, A. P. Kampf, T. Kopp, and D. Braak, Phys. Rev. B **96**, 024508 (2017).
[32] N. Wennerdal and M. Eschrig, Phys. Rev. B **95**, 024513 (2017).
[33] N. Mohanta and A. Taraphder, EPL (Europhysics Letters) **108**, 60001 (2014).
[34] F. Loder, A. P. Kampf, and T. Kopp, Scientific reports **5**, 15302 (2015).
[35] G. Cheng, M. Tomczyk, S. Lu, J. P. Veazey, M. Huang, P. Irvin, S. Ryu, H. Lee, C.-B. Eom, C. S. Hellberg, *et al.*, Nature **521**, 196 (2015).
[36] C. Brun, T. Cren, and D. Roditchev, Supercond. Sci. Technol **30**, 013003 (2016).
[37] H. Nam, H. Chen, T. Liu, J. Kim, C. Zhang, J. Yong, T. R. Lemberger, P. A. Kratz, J. R. Kirtley, K. Moler, P. W. Adams, A. H. MacDonald, and C.-K. Shih, Proc. Natl. Acad. Sci. USA **113**, 10513 (2016).
[38] T. Zhang, P. Cheng, W.-J. Li, Y.-J. Sun, G. Wang, X.-G. Zhu, K. He, L. Wang, X. Ma, X. Chen, Y. Wang, Y. Liu, H.-Q. Lin, J.-F. Jia, and Q.-K. Xue, Nature Physics **6**, 104 (2010).
[39] G. C. Menard, S. Guissart, C. Brun, R. T. Leriche, M. Trif, F. Debontridder, D. Demaille, D. Roditchev, P. Simon, and T. Cren, Nat. Comm. **8**, 2040 (2017).
[40] A. C. Potter and P. A. Lee, Phys. Rev. B **85**, 094516 (2012).
[41] L. Yan-Feng, W. Wen-Lin, Z. Yi-Min, D. Hao, L. Wei, W. Lili, H. Ke, S. Can-Li, M. Xu-Cun, and X. Qi-Kun, Sci. Bull. **62**, 852 (2017).
[42] See Supplemental Material at [URL] for more information, which includes Refs. 43,59 and 64-76..
[43] C. Lei, H. Chen, and A. H. MacDonald, to be published.
[44] C.-K. Chiu, J. C. Y. Teo, A. P. Schnyder, and S. Ryu, Rev. Mod. Phys. **88**, 035005 (2016).
[45] R. L. Hota, G. S. Tripathi, and J. N. Mohanty, Phys. Rev. B **47**, 9319 (1993).
[46] R. Patnaik and G. Tripathi, Solid State Commun. **112**,

669 (1999).
[47] M. Debessai, T. Matsuoka, J. J. Hamlin, W. Bi, Y. Meng, K. Shimizu, and J. S. Schilling, J. Phys.: Confer. Series **215**, 012034 (2010).
[48] J. Eisenstein, Rev. Mod. Phys. **26**, 277 (1954).
[49] G. P. Mikitik and Y. V. Sharlai, Phys. Rev. B **67**, 115114 (2003).
[50] D. Xiao, J. Shi, and Q. Niu, Phys. Rev. Lett. **95**, 137204 (2005).
[51] T. Thonhauser, D. Ceresoli, D. Vanderbilt, and R. Resta, Phys. Rev. Lett. **95**, 137205 (2005).
[52] M. Miasek, Phys. Rev. **130**, 11 (1963).
[53] J. E. Craven, Phys. Rev. **182**, 693 (1969).
[54] A. D. Zdetsis, E. N. Economou, and D. A. Papaconstantopoulos, J. Phys. F **10**, 1149 (1980).
[55] M. E. Woods and B. J. Hopkins, J. Phys. C **18**, 217 (1985).
[56] B. Slomski, G. Landolt, S. Muff, F. Meier, J. Osterwalder, and J. H. Dil, New J. Phys. **15**, 125031 (2013).
[57] J. H. Dil, F. Meier, J. Lobo-Checa, L. Patthey, G. Bihlmayer, and J. Osterwalder, Phys. Rev. Lett. **101**, 266802 (2008).
[58] L. Florian, P. K. Arno, and K. Thilo, J. Phys. Condens. Matter **25**, 362201 (2013).
[59] C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).
[60] M. Oshiki and E. Fukada, J. Mater. Sci. **10**, 1 (1975).
[61] D. E. Grupp and A. M. Goldman, Science **276**, 392 (1997).
[62] Z. Zhang, Q. Niu, and C.-K. Shih, Phys. Rev. Lett. **80**, 5381 (1998).
[63] M. Murakami and R. W. Vook, Crit. Rev. Solid State Mater. Sci. **11**, 317 (1983).
[64] P. Giannozzi, O. Andreussi, T. Brumme, O. Bunau, M. B. Nardelli, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, M. Cococcioni, N. Colonna, I. Carnimeo, A. D. Corso, S. de Gironcoli, P. Delugas, R. A. D. Jr, A. Ferretti, A. Floris, G. Fratesi, G. Fugallo, R. Gebauer, U. Gerstmann, F. Giustino, T. Gorni, J. Jia, M. Kawamura, H.-Y. Ko, A. Kokalj, E. Kkbenli, M. Lazzeri, M. Marsili, N. Marzari, F. Mauri, N. L. Nguyen, H.-V. Nguyen, A. O. de-la Roza, L. Paulatto, S. Ponc, D. Rocca, R. Sabatini, B. Santra, M. Schlipf, A. P. Seitsonen, A. Smogunov, I. Timrov, T. Thonhauser, P. Umari, N. Vast, X. Wu, and S. Baroni, J. Phys. Condens. Matter **29**, 465901 (2017).
[65] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter **21**, 395502 (19pp) (2009).
[66] A. Dal Corso, Comput. Mater. Sci **95**, 337 (2014).
[67] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[68] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14251 (1994).
[69] G. Kresse and J. Furthmüller, Comput. Mater. Sci **6**, 15 (1996).
[70] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[71] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[72] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).
[73] "Bismuth telluride (bi2te3) crystal structure, chemical bond, lattice parameters (including data for related compounds): Datasheet from landolt-brnstein - group iii condensed matter volume 41c: "non-tetrahedrally bonded elements and binary compounds i" in springermaterials,".
[74] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nat. Phys. **5**, 438 (2009).
[75] "Srtio3 crystal structure, lattice parameters: Datasheet from landolt-brnstein - group iii condensed matter volume 41e: "ternary compounds, organic semiconductors" in springermaterials,".
[76] K. Motizuki, H. Ido, T. Itoh, and M. Morifuji, *Electronic Structure and Magnetism of 3d-Transition Metal Pnictides*, Springer Series in Materials Science (Springer Berlin Heidelberg, 2009).