

I propose to develop and implement a frame of understanding complex structural distortions in topologically relevant materials. Successful execution of this approach will lead to new materials discovery and generate new methods for electronic band structure engineering.

Introduction: Linking desired physical properties to structural motifs is a fundamental goal in solid-state chemistry. As we will see, topological semimetals are exemplars to this goal: ultrahigh mobility electrons arising from linear band crossings can be derived from specific structural motifs, further predicted from basic electron counting rules¹. Previous work regarding topological materials has largely focused on systematically scanning the thermodynamic stability of compositions in particular space groups, followed by selected synthesis of the most promising candidates. More recently, scientists have explored how slight perturbations of topological systems can induce charge density waves through structural modulations rationalized via electronic considerations.² That is, seemingly simple chemical substitutions used as n- or p-type dopants, aimed to adjust the Fermi energy to lie in a precise electron state.

Changing the composition of a structure may induce a structural change, such as a Peierls distortion, which would open a up bandgap at the Fermi energy. Further, exactly *how* a given structural transition navigates its potential energy surface to form such specific distortions is largely unexplored in the literature. Finally, even if such chemical substitution does not significantly alter a structure, development of predictive strategies for diversifying the possibilities of elemental substitution should be developed. Exploring synthetic control over such distortions in topological materials can provide one such prescription to these issues. Thus, understanding how such distortions lead to thermodynamic favorability, paired with how such distortions alter physical properties, may then open a playbook for “band engineering” where finely tuning composition can gap out unwanted bands from the Fermi surface.

Background: Topological materials can be well understood through the Zintl-Klemm concept: an electron counting method where transfer of electrons is assumed from the most electropositive element to the most electronegative element in a crystal structure. The remaining atoms then form covalent networks to reduce the total thermodynamic energy of the system. In Figure 1a, a Walsh diagram shows the thermodynamic stability of a Te_3 chain as a function of bond angle. The linear geometry is found to be stabilized at 22 electrons, the third level, due to less overlap of anti-bonding interactions. In extended solids, it would then be predicted that linear chains form when there are 7 electrons per chain atom. Such is the case in UTe_2 , seen in Figure 1b, a promising candidate host for the sought-after Majorana quasi-particle.¹ Each uranium is found to be in the 3+ oxidation state and transfers two electrons to the nearest tellurium sites, forming what can be thought of as $[\text{UTe}]^+$ slabs and a linear Te^- chain. As a result, the geometry enforces a linear crossing at the Fermi energy, shown in Figure 1c. Doubling of the unit cell, when considering 2 atoms per unit cell, folds the band structure back on itself creating a linear band crossing located at the Fermi energy.

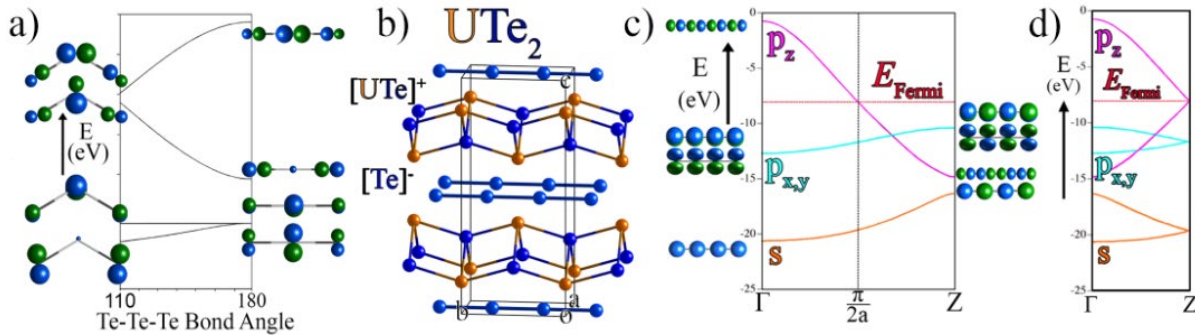


Figure 1. **a)** A Walsh diagram of a Te_3 molecular unit. **b)** The unit cell of UTe_2 , a topological superconductor containing linear chains. **c)** The resulting band structure for an isolated linear chain of Te^- ions. A linear crossing at the Fermi energy occurs halfway between the Γ and Z points. **d)** A folded band structure, arrived at by doubling the unit cell, forming a Dirac node at the Fermi energy.

Proposal: Derivation from ideal electron counts in such covalent networks can lead to a structural distortion. In the classical example of a linear chain of atomic orbitals, a half-filled band will favor dimerization, leading to differing bond lengths, opening a band gap at the Fermi energy. However, recent investigations have found, counterintuitively, that such distortions can lead to improved topological band

structures or high-mobility electrons. Despite a structural modulation in the square-net layer, which can be viewed as a two-dimensional linear chain, NdTe₃ exhibits ultra-high mobility electrons and anomalous quantum oscillation behavior¹. *Moreover, the distorted square nets in GdSb_{0.46}Te_{1.48} was recently shown to gap out trivial band crossings, “cleaning” the band structure by retaining the screw axis associated with its structural distortion.*²

For my analysis of similar systems, I will utilize recent adaptations of Density Functional Theory (DFT) outputs that establish direct links between local features in solid state compounds and their contribution to electronic and steric favorability. Specifically, the reversed applied Molecular Orbital (raMO) analysis aims to fit tight-binding parameters from DFT band structure calculations. As a result, DFT-calibrated molecular orbital diagrams are visualized to explain formation of closed-shell configurations (see Figures 1a) and c)). Parallel with this, DFT-Chemical Pressure (DFT-CP) resolves local packing frustrations that can arise within dense atomic packings, from which the role of atomic size can be assessed. Utilization of both these computational analyses can explain why a structure may obey or deviate from predictive bonding schemes such as the Zintl–Klemm concept.³ Both raMO and DFT-CP software packages are freely available via the GNU Public License and will be used in this work. I will also synthesize and structurally as well as electronically characterize the targeted compounds.

Therefore, I will employ an iterative approach of experiment and theory to implement a frame of understanding structural distortions in topological motifs, targeting the following **research objectives**:

1. *Determination* of topological systems in which unexpected electron counts or steric packing frustrations may favor charge density wave formation.
2. *Synthesis* of candidates, as well as detailed structural and physical characterization of materials.
3. *Demonstration* of band engineering through the tuning of new superstructures guided by theoretical analysis.

Intellectual Merit: Princeton University offers many unique multidisciplinary approaches needed to study topological materials. In the Schoop laboratory, I have access to core instruments needed for this investigation, including furnaces for solid-state synthesis, a single-crystal X-ray diffractometer for materials characterization, a magnetic properties measurement system, and a physical property measurement system with a dilution fridge. Through NSF supported opportunities, such as the Princeton Center for Complex Materials (PCCM), frequent collaborations will be drawn through an interdisciplinary research group focusing on topological quantum matter. Specifically, the Department of Physics offers many avenues for collaborative work in physical properties characterization with Dr. Nai Phuan Ong, Dr. Ali Yazdani, and Dr. Sanfeng Wu. There are also many opportunities through the NSF-funded Imaging and Analysis Center which provides access to instruments such as the scanning electron microscope.

Frequent collaborations outside of Princeton University will also be utilized. So far, *single-crystal diffraction data obtained for a linear chain system indicate missed satellite peaks with a modulation vector $q = 0.06a^*$, indicating a massive 50/3 supercell periodicity. Despite prediction of such a distortion ruining the metallicity of the structure, electrical transport data suggests that the system remains metallic.* To this end, a proposal has been written and sent to Dr. Yusheng Chen at Argonne National Laboratory, hopefully to be accepted for next cycle in March of 2022. Additionally, the Schoop laboratory frequently collaborates with scientists at Helmholtz-Zentrum Berlin such as Dr. Andrei Varykhalov at the BESSY II beamline for angle-resolved photoemission spectroscopy. Looking ahead, probing the band structure of a crystal related to this project may significantly improve the impact of my investigations.

Broader Impacts: The predictive framework I develop will open paths to tailoring band structure through composition, allowing for more control of physical properties used in technological applications. In the future I will expand to other structural motifs such as the square- and Kagome-nets. Finally, visualization tools, like raMO, have chemical education implications for use in NSF-funded operations, such as PCCM’s Princeton University Materials Academy.

References:

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