Large Thermopower in topological crystalline insulating perovskite ThTaN$_3$

Kwan-Woo Lee

1Division of Display and Semiconductor Physics & 2Department of Applied Physics, Graduate School, Korea Univ., Sejong

Collaborations

Myung-Chul Jung (KU)  W. E. Pickett (UC Davis)

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Introduction

- Topological crystalline insulator (TCI)
- Theoretical predictions and observations of TCI
- Calculation Methods

Results

- Electronic structures
- Analysis of topological characters
- Thermoelectric properties

Summary
Topological crystalline insulators

- TCI
  - trivial $Z_2$ number (cf., $Z_2=1$ for ordinary $Z_2$ TIs)
  - even crossings in a hybrid Wannier charge center plot
  - zero Chern number, but **nonzero mirror Chern number**
    \[ C_M = (C_+ - C_-)/2 \]
    for Bloch eigenstates with eigenvalues $\eta = \pm i$

- SOC is not a requirement in TCI, but will affect the gap size.

- $C_n + \text{TR sym. in 3D } (n=4, 6)$
  - tetragonal lattice

- only $C_{nv} \ (n=3, 4, 6)$
  - Cn + TR sym. in 3D (n=4, 6)
Theoretical predictions of TCI

**RockSalt IV-VI semiconductor**

- SnTe, SnS/SnSe
  - Hsieh et al. (MIT), Nat. Commun. **3**, 982 (2012);
- PbPo
  - Kang and Min (Postech), PRB **93**, 041104(R) (2016).
- Monolayer of PbSe etc.

**Transition metal oxides**

- Pyrochlore oxide A$_2$Ir$_2$O$_7$
  - Kargarian & Fiete (U. of Texas, Austin), PRL **110**, 156403 (2012).
- Orthorhombic Perovskite SrIrO$_3$
- Antiperovskite
  - Hsieh et al. (MIT), PRB **90**, 081112(R) (2014).

➢ Protected by mirror sym.

➢ Protected by mirror sym even for no TR & showing a crucial role of SOC
Full-Heusler

Pham & Li (Australia), PRB 95, 115124 (2017).

Graphen multilayers

Kindermann (Georgia Tech.), PRL 114, 226802 (2015).

➤ Note: TCI can coexist with other topological properties.

Rauch et al., PRL 112, 016802 (2014).
Experimental Observations of TCI

IV-VI semiconductors of (Pb,Sn)Te/Se

- Observed a double Dirac cone for the system with the mirror Chern number of 2.
- Breaking the surface states by removing crystalline symmetries.

Tanaka et al. (Tohoku Univ.), Nat. Phys. 8, 800 (2012).
Dziawa et al. (Poland), Nature Mater. 11, 1023 (2012).

- Okada et al. (Tohoku Univ. & Princeton Univ.) Science 341, 1496 (2013).
Cubic perovskite nitride ThTaN$_3$

- Narrow gap semiconductor
- A sizable spin-orbit coupling in Ta ion is expected.
- A rare cubic perovskite nitride: itinerant hole or electron doping is expected to be much easier than in oxides.


- Space group: Pm$\bar{3}$m (#221) with $C_{4v}$ (mirror +4-fold rotation) sym.
- Lattice constant of $a = 4.02$ Å
Calculation Methods

- All calculation results are based on Wien2k.
  - 21x21x21 \( k \)-mesh
  - \( R_{mt}K_{max} = 7 \)
  - APW radii of Th (2.4), Ta (2.0), and N (1.7) (in units of a.u.)
  - GGA & GGA+SOC

- Wannier function approach (Wannier90)
  - Basis: Ta 5d, N 2p, and Th 6d, 5f

- Surface state calculation
  : WannierTools, based on the Green function method

- Thermoelectric property
  : Boltztrap, based on the semiclassical Boltzmann transport theory
    with a constant relaxation time approximation
  - dense \( k \)-mesh: 60000 \( k \)-points within IBZ
Even in GGA, this system is nearly gapped.
The top of the valence bands is N 2p, whereas the bottom of the conduction bands is the Ta t_{2g}.
The Ta d orbitals undergo a substantial spin-orbit coupling (SOC), splitting the 3-fold bands on the either side into a doublet and singlet at the zone center.

- SOC results in band inversion and enhancing the energy of 150 meV.
- This feature suggests a nontrivial topological character.
The HWCC for half of the BZ on the mirror plane shows an even crossing and trivial $Z_2$ indices $0;(000)$. The trivial indices are also obtained from the parties of all occupied bands at the TRIMs.

[Question] Is this system topologically trivial?
The function is obtained from the Green function approach.

In both terminations, two pairs of surface bands crossing the gap appear at the zone center.

The right columns show the spin textures (red arrows) on the cuts of the Dirac cones.
Breaking symmetries

Breaking both the C₄ rotation and mirror symmetries removes the surface states completely.
Nature of the topological character

- It indicates that this system is a TCI protected by the $C_4$ rotation + mirror symmetries, as in the antiperovskite.
- These two pairs of surface bands indicates the mirror Chern number of 2.
- The two Dirac cones concurrently emerge at the zone center.

\[ |C_M| = \frac{C_+i - C_-i}{2} = 2 \]
for Bloch states with eigenvalues $\eta = \pm i$. 

- The mirror Chern number:
Seebeck coefficients $S(T)$ in GGA+SOC

- $S(T)$ is roughly doubled by SOC.
- A very high value of $\sim 400 \mu V/K$ is at 150 K for a small hole.
- For low doping level $\sim 10^{-4} - 10^{-6}$ carriers/f.u., it retains excellent thermoelectric performance denoted the dashed lines in (b) & (c).
TCI & thermoelectric properties

- No direction relation between thermoelectric (bulk) and topological (surface) properties
- Only commonality is a narrow band gap.
- SOC leads to considerable changing in dispersion around $E_F$, thus providing a steep DOS (often signal of large thermopower).
- It happens in this system.

The surface conductance leads to an anomalous Seebeck effect that can be tuned by engineering the size and shape of the sample.

⇒ a new frontier in topological materials.
The perovskite ThTaN₃ is a TCI with a large gap of 150 meV and the mirror Chern number number of 2.

ThTaN₃ has a large Seebeck coefficient with a maximum value of \( \sim 400 \mu V/K \).

ThTaN₃ is not only a TCI, but also displays highly favorable thermoelectric properties.

It may provide new possibilities for platforms for engineering devices with larger figures of merits.