Infrared Optical Properties of Quasi-1D Topological Insulators: Bi_4Br_4 and Bi_4I_4

Quasi-1D Topological Quantum Materials Workshop • 6 January 2023

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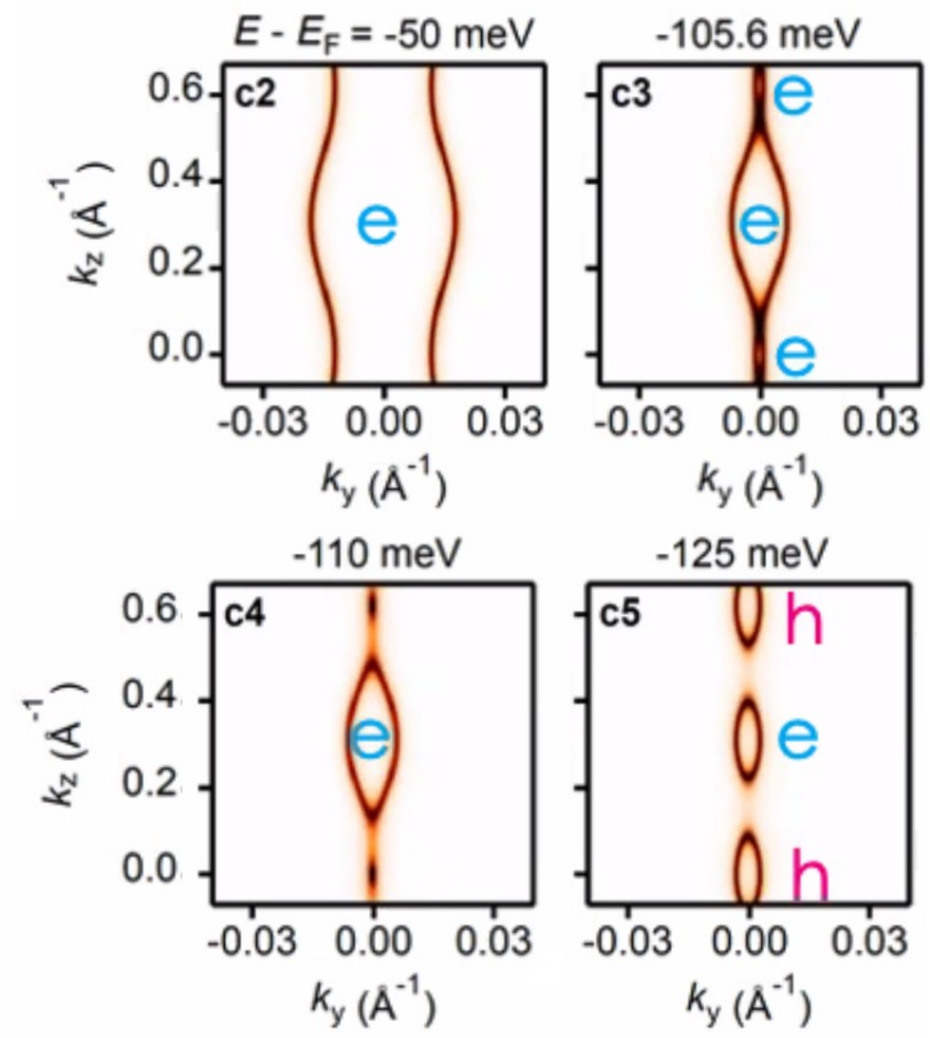
Why Quasi-1D Materials?

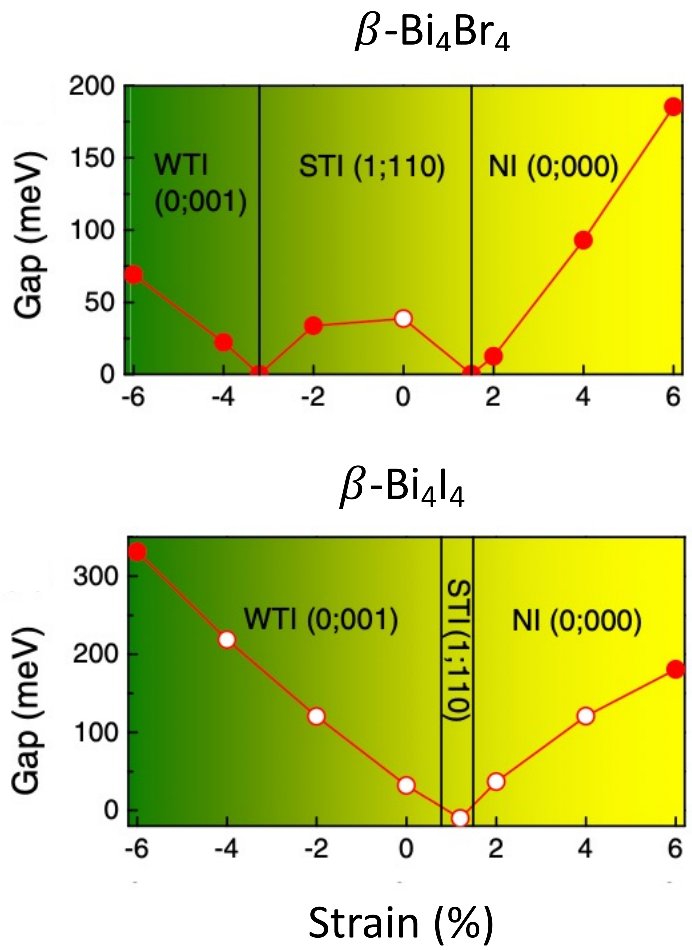
- We want to realize exotic states
- Weak TIs[1,2]
  - Even numbers of Dirac cones on some surfaces
  - First realized in β-Bi_4I_4
- HOTIs[3,4]
  - Edge state in α-Bi_4Br_4 and α-Bi_4I_4
- Luttinger liquids and exciton condensates

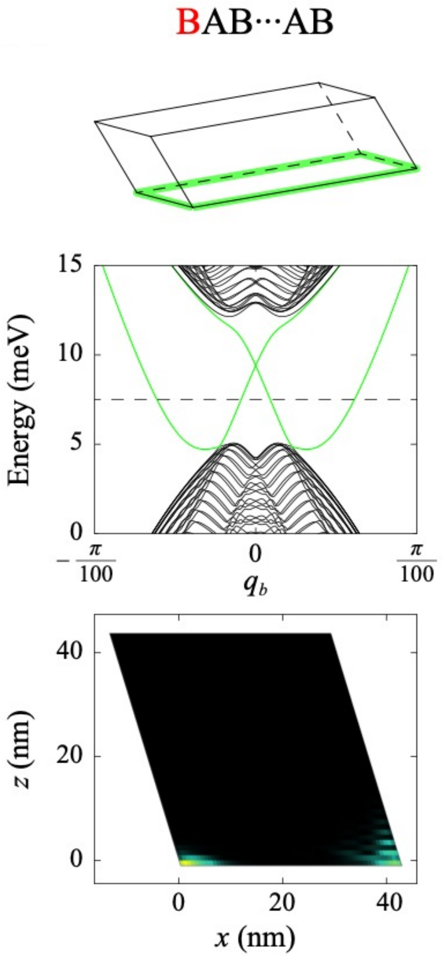
1. C.C. Liu, et al. PRL **116**, 066801 (2016)
2. R. Noguchi, et al. Nature **566,** 518 (2019)
3. C. Yoon, et al. arXiv 2005.14710 (2020)
4. J. Huang, et al. PRX **11**, 031042 (2021)



Topology in Quasi-1D Materials and Bi_4X_4

- How to realize a weak TI?
  - Stack weakly coupled QSH layers
    - D.F. Mross, et al. PRL **116**, 036803 (2016)
  - Quasi-1D material
    - C.C. Liu, et al. PRL **116**, 066801 (2016)
- Higher order TIs
  - F. Zhang, et al. PRL **110**, 046404 (2013)
  - W. A. Benalcazar, et al. Science **357**, 61 (2017)
  - C. Yoon, et al. arXiv 2005.14710 (2020)





Van der Waals Materials

- Direction-dependent bond strength leads to natural cleavage planes
- Good cleavage planes makes for easy access to surface and edge states
- Many materials are stacked 2D layers
- Relatively few in stacks of 1D chains
  - Bi_4X_4, $TaSe_3$, $TaTe_4$, Nb_2Se_4, $NbCl_4$, MoI_3

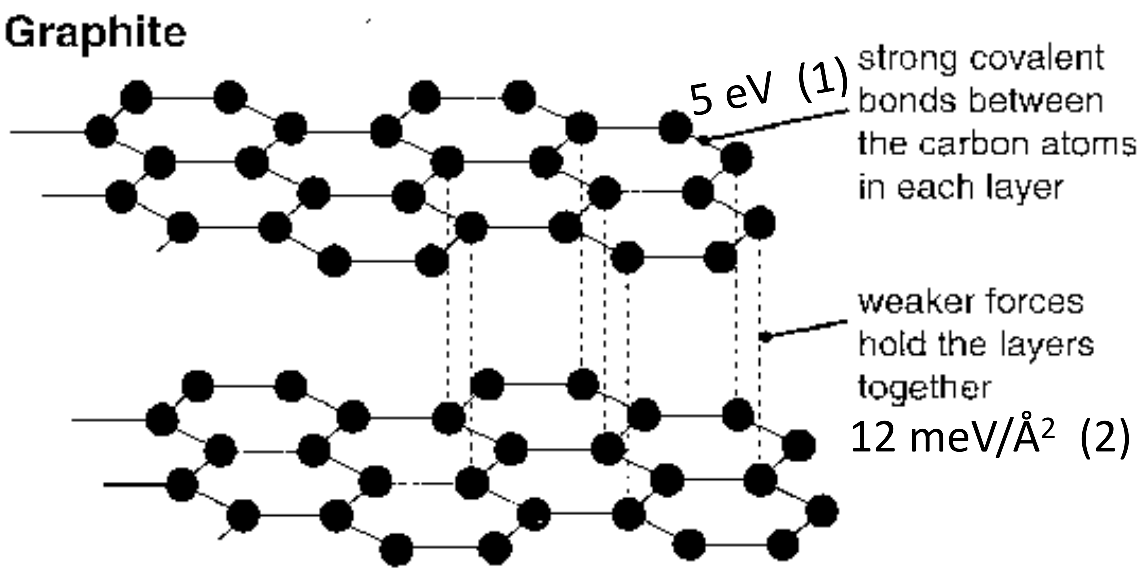


Image from J. Clark, Chemistry Libretexts, 14.4 (2021). CC BY-NC-SA 3.0.

1. D. Brenner, et al. JPCM **14** 783 (2002)
2. Z. Liu, et al. PRB **85**, 205418 (2012)

Structure of Quasi-1D Materials: Bi_4X_4

- Bi_4Br_4 and Bi_4I_4 are 1D chains that align to form 3D materials[1,2,3]
- Two natural cleavage planes
  - (001) surface: trivial insulator[1]
  - (100) surface: weak/strong TI[1]

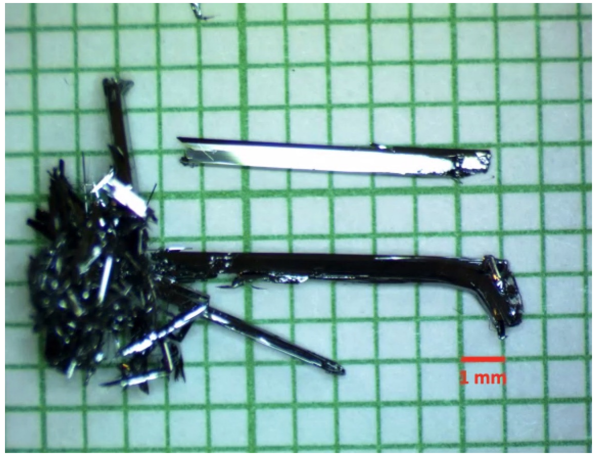
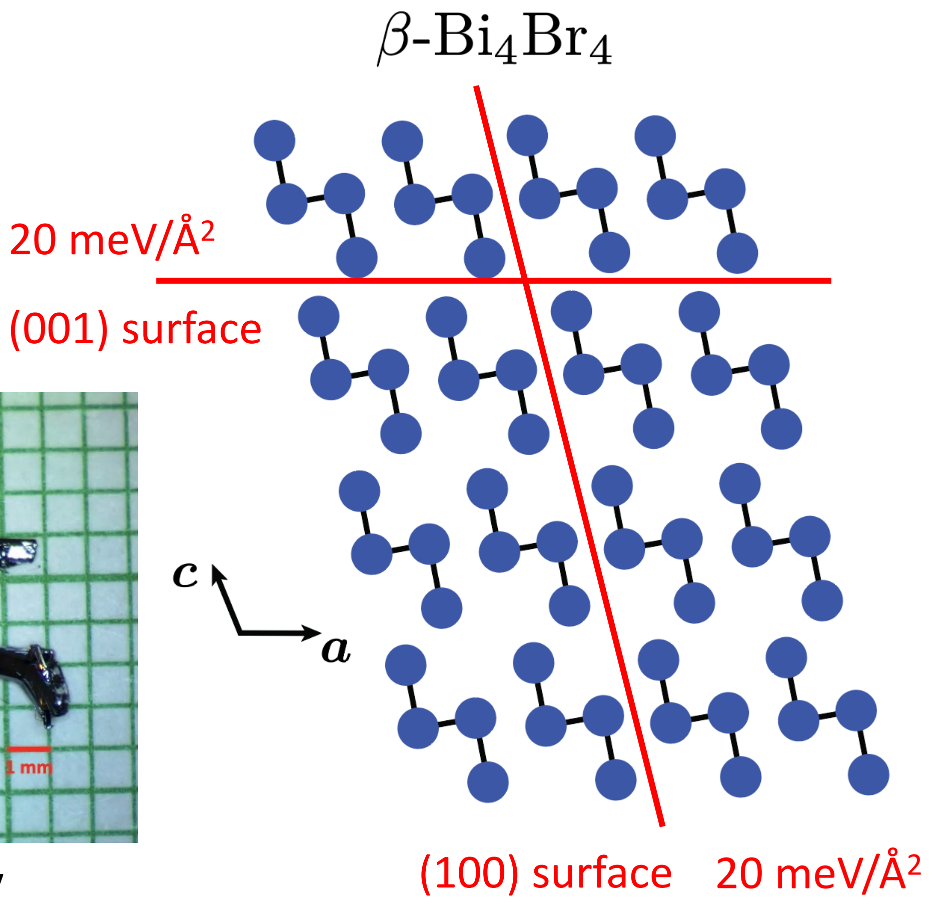
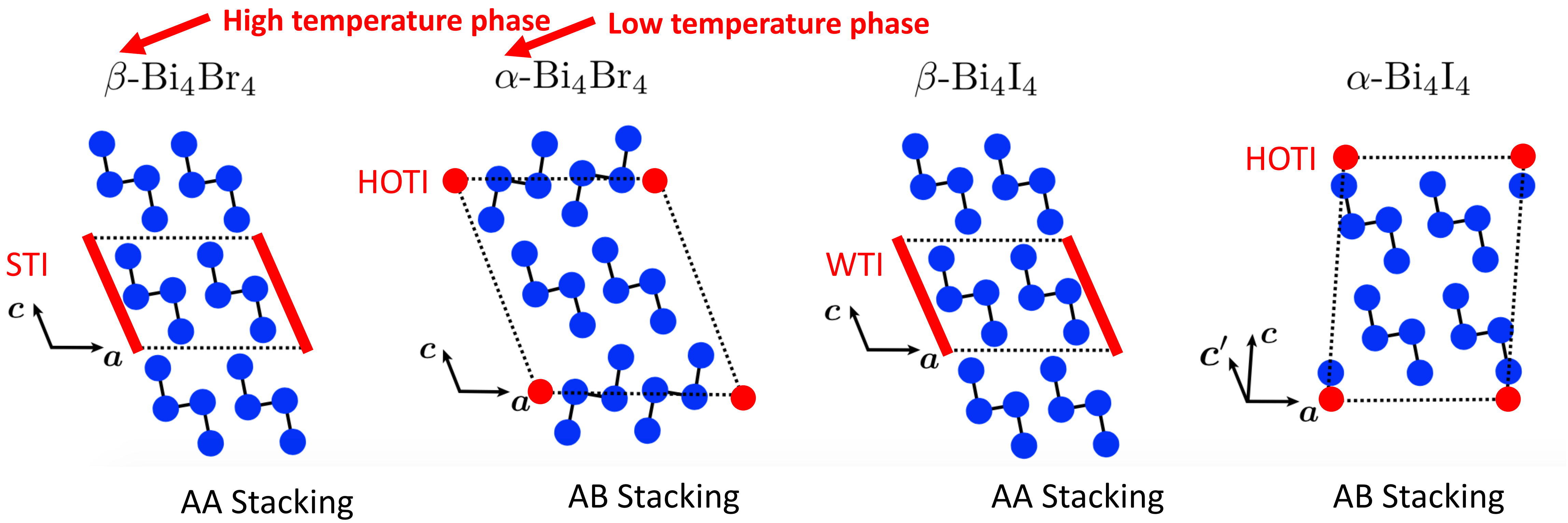


Image courtesy of Bing Lv



1. C.C. Liu, et al. PRL **116**, 066801 (2016)
2. C. Yoon, et al. arXiv 2005.14710 (2020)
3. H. G. von Schnering, et al Z. Inorg. Chem. 438, **37** (1978).
   H. von Benda, et al. Z. Inorg. Chem. 438, **53** (1978).

Phases of Bismuth Halides

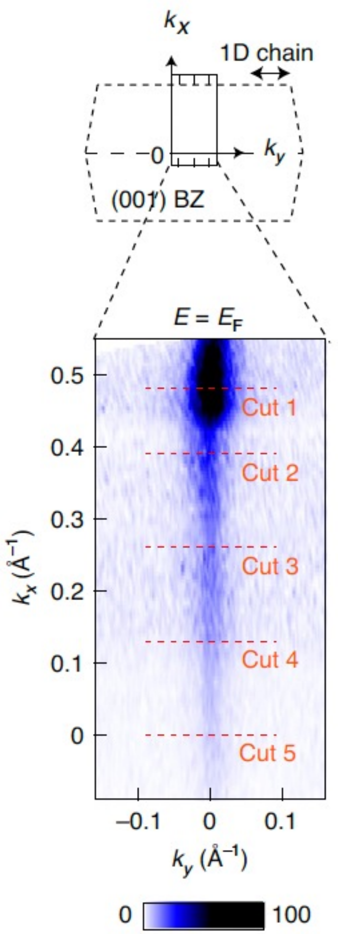


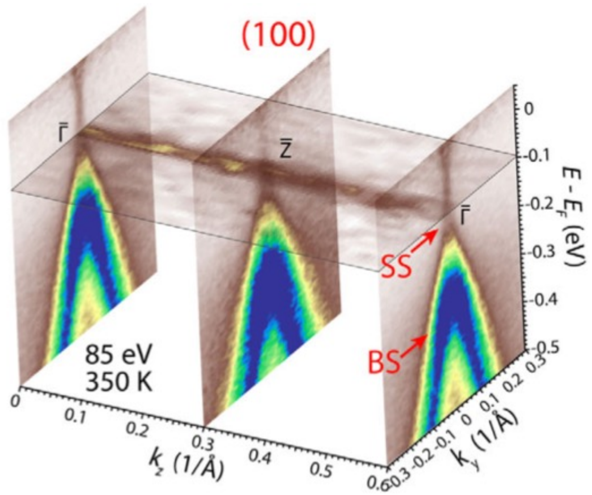
1. C.C. Liu, et al. PRL **116**, 066801 (2016)
2. C. Yoon, et al. arXiv 2005.14710 (2020)
3. R. Noguchi, et al. Nature **566,** 518 (2019)

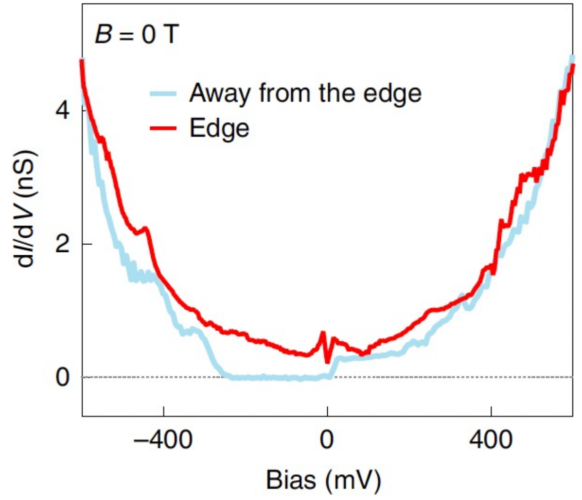
STM and ARPES Measurements

- Conclusive evidence for weak TI on (100) surface[1,2]
- STM evidence of a QSH state on edges[3]
- Supporting evidence for HOTI on edges[4]
    - Limited by spatial resolution of ARPES

1. R. Noguchi, et al. Nature **566,** 518 (2019)
2. J. Huang, et al. PRX **11**, 031042 (2021)
3. N. Shumiya, et al. Nat. Mater. **21**, 1111 (2022)
4. R. Noguchi, et al. Nat. Mater. **20**, 473 (2021)



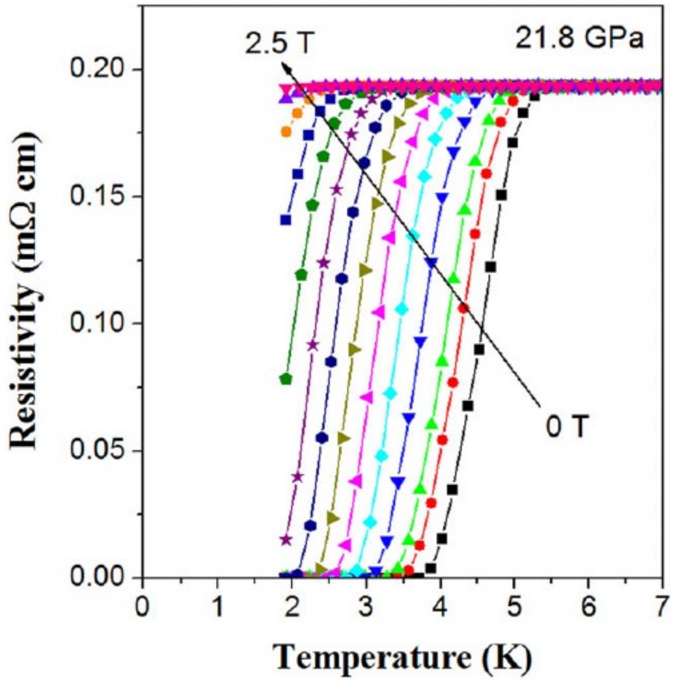


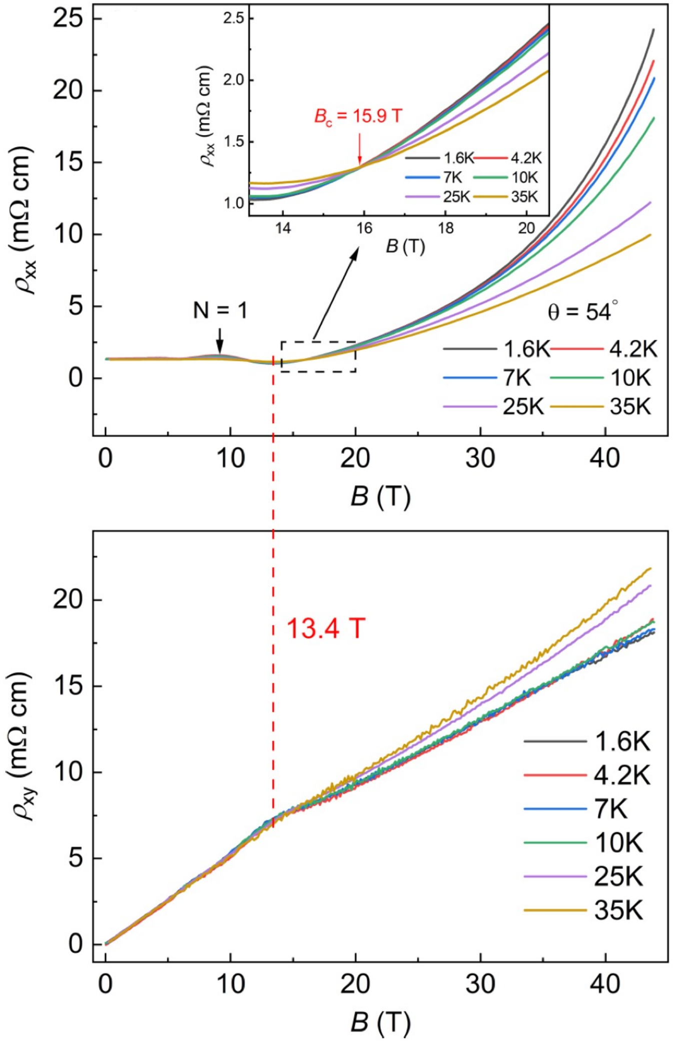


Transport Measurements

- Pressure induced superconductivity[1,2]
- Field-induced metal-insulator transition[3,4]

1. X. Wang, et al. Phys. Rev. B **98**, 174112 (2017)
2. Y. Qi, et al. Npj Q. Mater. 3, **1** (2018)
3. D. Y. Chen, et al. Phys. Rev. Mater. **2**, 114408 (2018)
4. P. Wang, et al. Phys. Rev. B **103**, 155201 (2021)

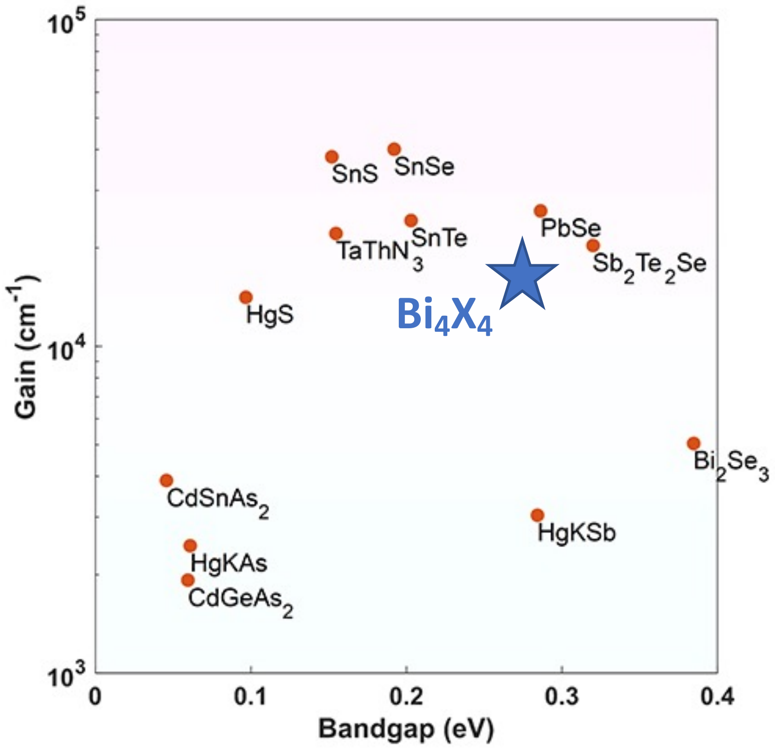




Why Optics?

- Optical responses can both characterize materials and be used to create devices

1. Anisotropic and "giant" bulk response[1]
   - 10^4/cm at the band edge
2. Signatures for surface and edge states
   - Elliptic Dirac cone
3. Quasi-1D surface plasmon polaritons



1. H. Xu, et al. Phys. Chem. Lett. **11**, 6119 (2020)

Outline

- Introduction ✓
- Model and methods
- Bulk and (100) side surface optics
- Surface plasmon polaritons
- Conclusion

Methods

Our group's previous work in: C. Yoon, et al. arXiv 2005.14710 (2020)

Structure

↓ First-principles DFT

MLWF tight-binding model

↓ Best-fit nearest-neighbor tight-binding model

The current work

Hamiltonians and velocity operators

↓ Integrate Kubo formula

Optical conductivity

↓ Textbook formulas

Optical response properties

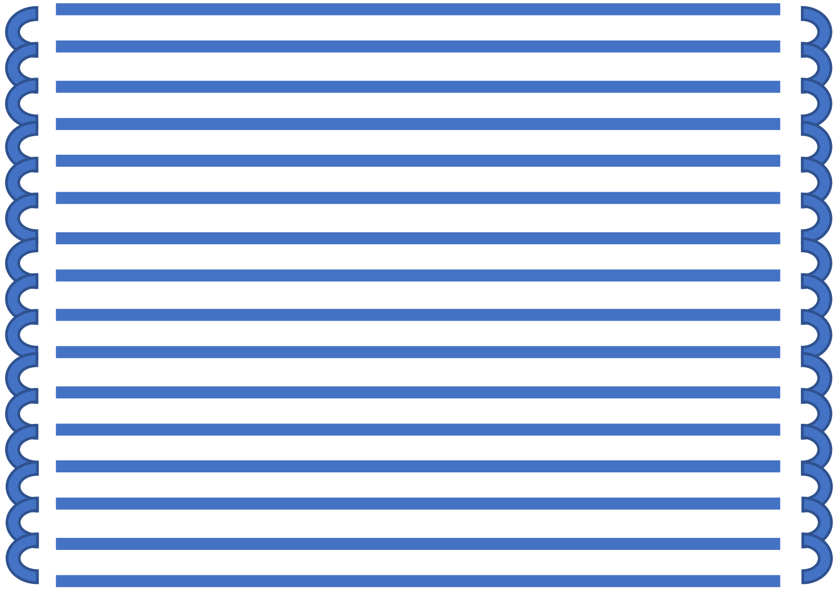
Model: β Bulk

- Construct layer Hamiltonians
  - All nearest-neighbor hopping terms that preserve inversion symmetry

$$H_L = M\sigma_z + D + t_a\sigma_y(\sin(q_1) + \sin(q_2)) + t_b\sigma_x s_z \sin(q_2 - q_1)$$
$$M = m_0 + m_a(\cos(q_1) + \cos(q_2)) + m_b \cos(q_2 - q_1)$$
$$D = d_0 + d_a(\cos(q_1) + \cos(q_2)) + d_b \cos(q_2 - q_1)$$

- Construct bulk Hamiltonians
  - Add inter-layer transfer terms that respect inversion symmetry

$$H_\beta = H_L + 2(d_c + m_c\sigma_z)\cos(q_3) + 2t_c\sigma_x s_y \sin(q_3)$$



1. C. Yoon, et al. arXiv 2005.14710 (2020)

Model: α Bulk

- Dimerizes
- SSH-like model

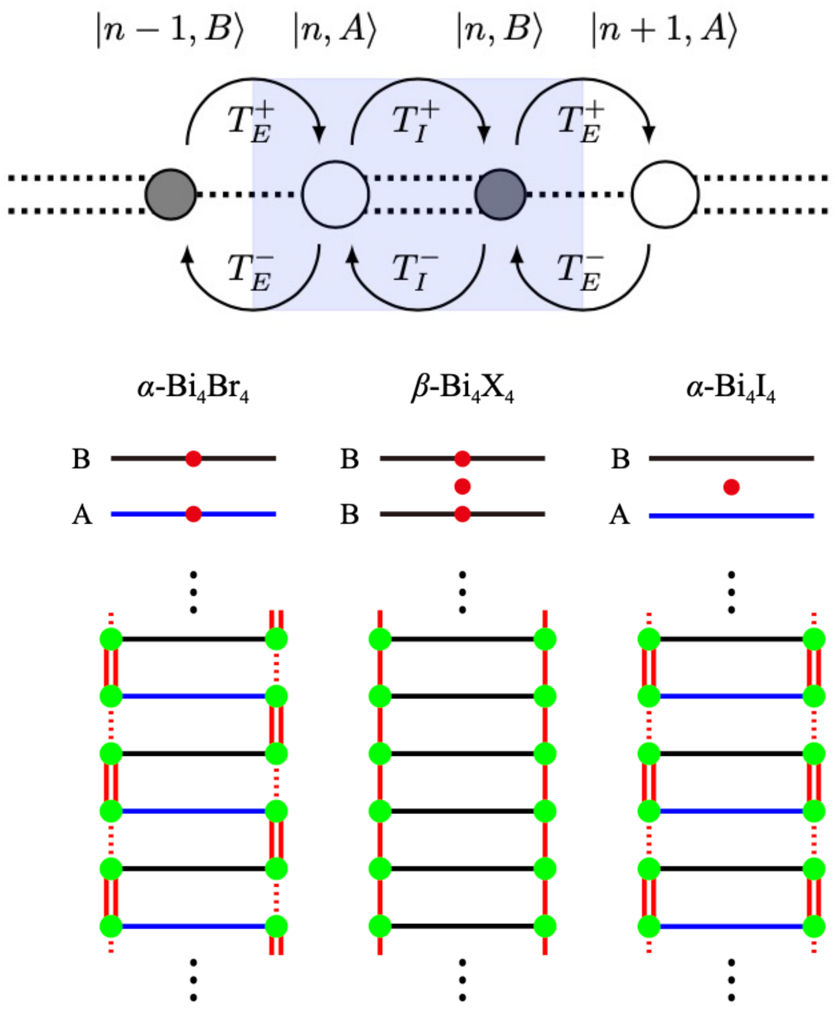
$$H_6^+ = \begin{pmatrix} H^+ & T_I^- & 0 & 0 & 0 & 0 \\ T_I^+ & H^- & T_E^- & 0 & 0 & 0 \\ 0 & T_E^+ & H^+ & T_I^- & 0 & 0 \\ 0 & 0 & T_I^+ & H^- & T_E^- & 0 \\ 0 & 0 & 0 & T_E^+ & H^+ & T_I^- \\ 0 & 0 & 0 & 0 & T_I^+ & H^- \end{pmatrix}$$

- Layers

$$H^\pm = H_L \pm (t\sigma_x + t'\sigma_y s_y)$$

- Hoppings

$$T_I^\pm = (d_c + m_c\sigma_z) \pm i(\sigma_x s_y t_c)$$
$$T_E^\pm = (d'_c + m'_c\sigma_z) \pm i(\sigma_x s_y t'_c)$$



Model: Edges and Side Surfaces

- Impose topological boundary conditions on the bulk[1,2]

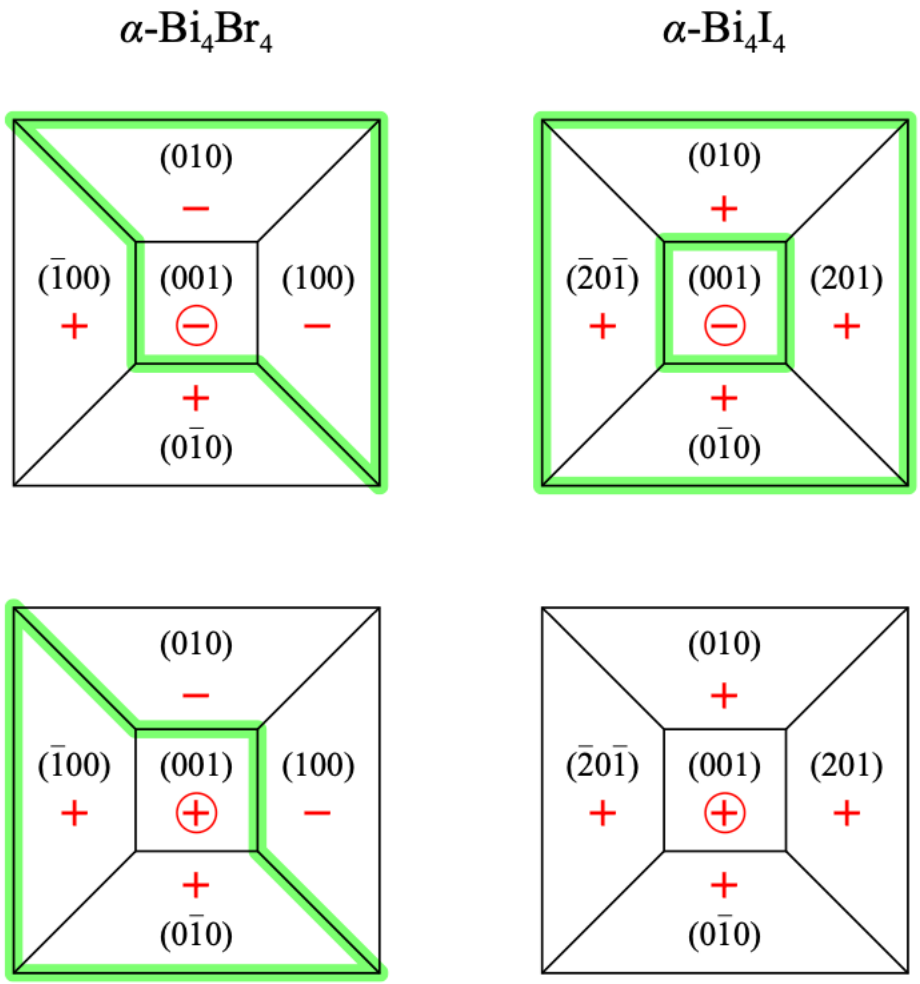
$$h_{\beta\text{-I}} = h_E + 2d_c\mathbb{1} + 2\xi t_c s_y q_c$$

$$h_{\alpha\text{-I}} = h_E + \xi t \tau_z + (d_c\tau_x + d'_c(\tau_x\cos(q_c) + \tau_y\sin(q_c))) + \xi s_y(t_c\tau_y - t'_c(\tau_y\cos(q_c) - \tau_x\sin(q_c))$$

- Edge Hamiltonian
  - Consistent with surface and bulk
  - Onsite and hopping terms

$$h_E = (d_0 - 2d_a + d_b)\mathbb{1} + \xi t_b s_z q_b$$

1. F. Zhang, et al. PRL **110**, 046404 (2013)
2. C. Yoon, et al. arXiv 2005.14710 (2020)



Kubo Formula Integration

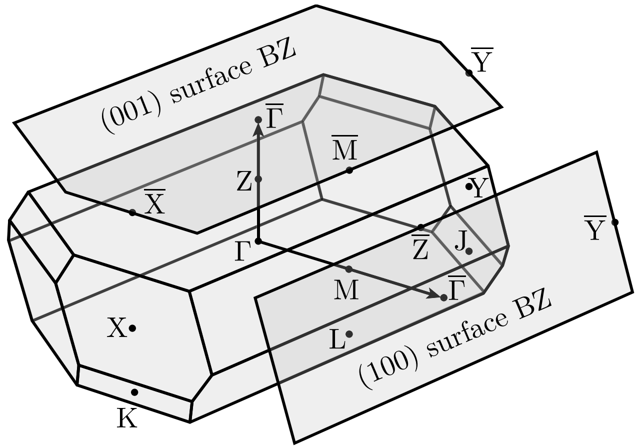
- Kubo formula

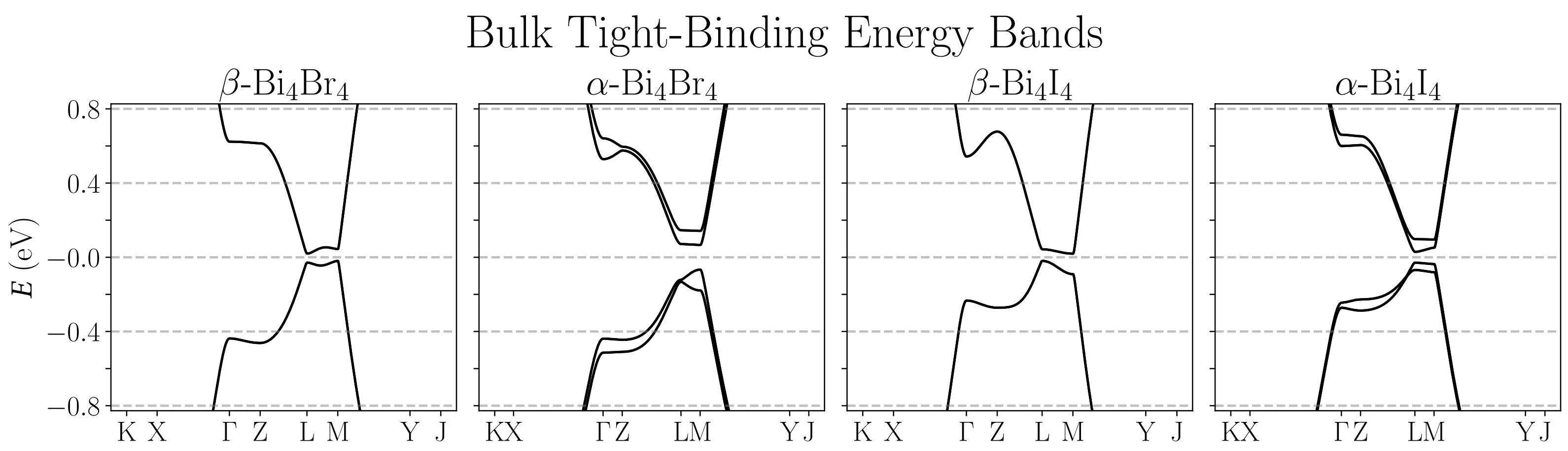
$$\sigma_{\mu\nu} = i\frac{e^2}{\hbar}\sum_{s,s'}\int_{\mathrm{BZ}}\frac{d\boldsymbol{k}}{(2\pi)^{\mathrm{dim}}}\frac{1}{\epsilon_{s'}-\epsilon_s}\frac{\langle s,\boldsymbol{k}\left|\hbar\frac{\partial\mathcal{H}}{\partial k_\mu}\right|s',\boldsymbol{k}\rangle\langle s',\boldsymbol{k}\left|\hbar\frac{\partial\mathcal{H}}{\partial k_\nu}\right|s,\boldsymbol{k}\rangle}{\hbar\omega-(\epsilon_{s'}-\epsilon_s)+i\eta}$$

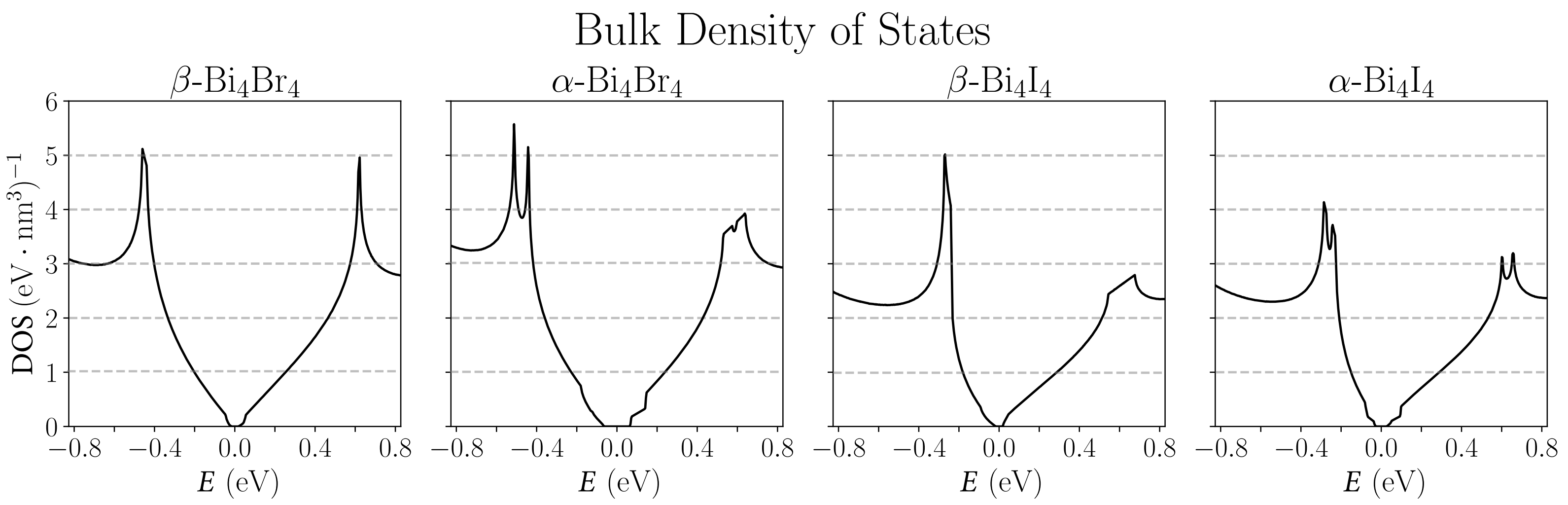
- Numerically integrate
  - Low temperature, low scattering rate limit
    - Need many points 10^8-10^9 points to converge
  - Only some regions of the Brillouin zone are relevant (the Z to M line)
  - Method
    - Uniformly sample Brillouin zone
    - Recursively refine over regions with energy conserving transitions

Bulk Band Structures

- Bi_4X_4 are bulk insulators
- The energy scale is the IR
- Low-energy physics is on the Gamma-Z-M plane
  - Suggests there will be anisotropic optics

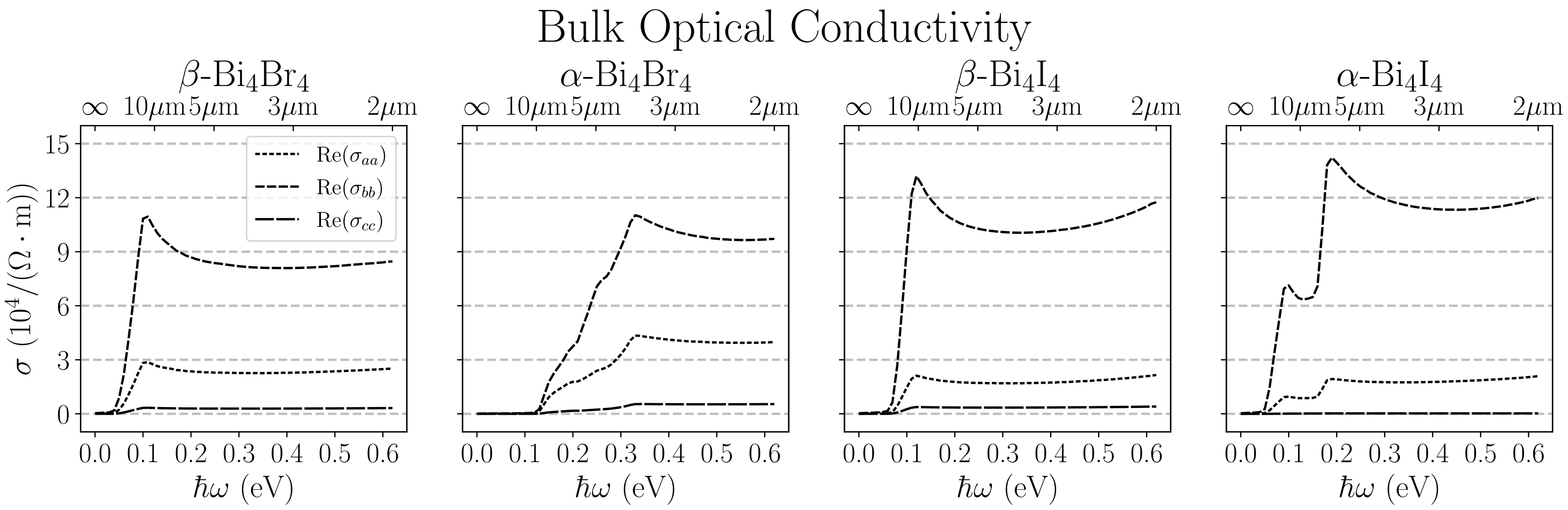






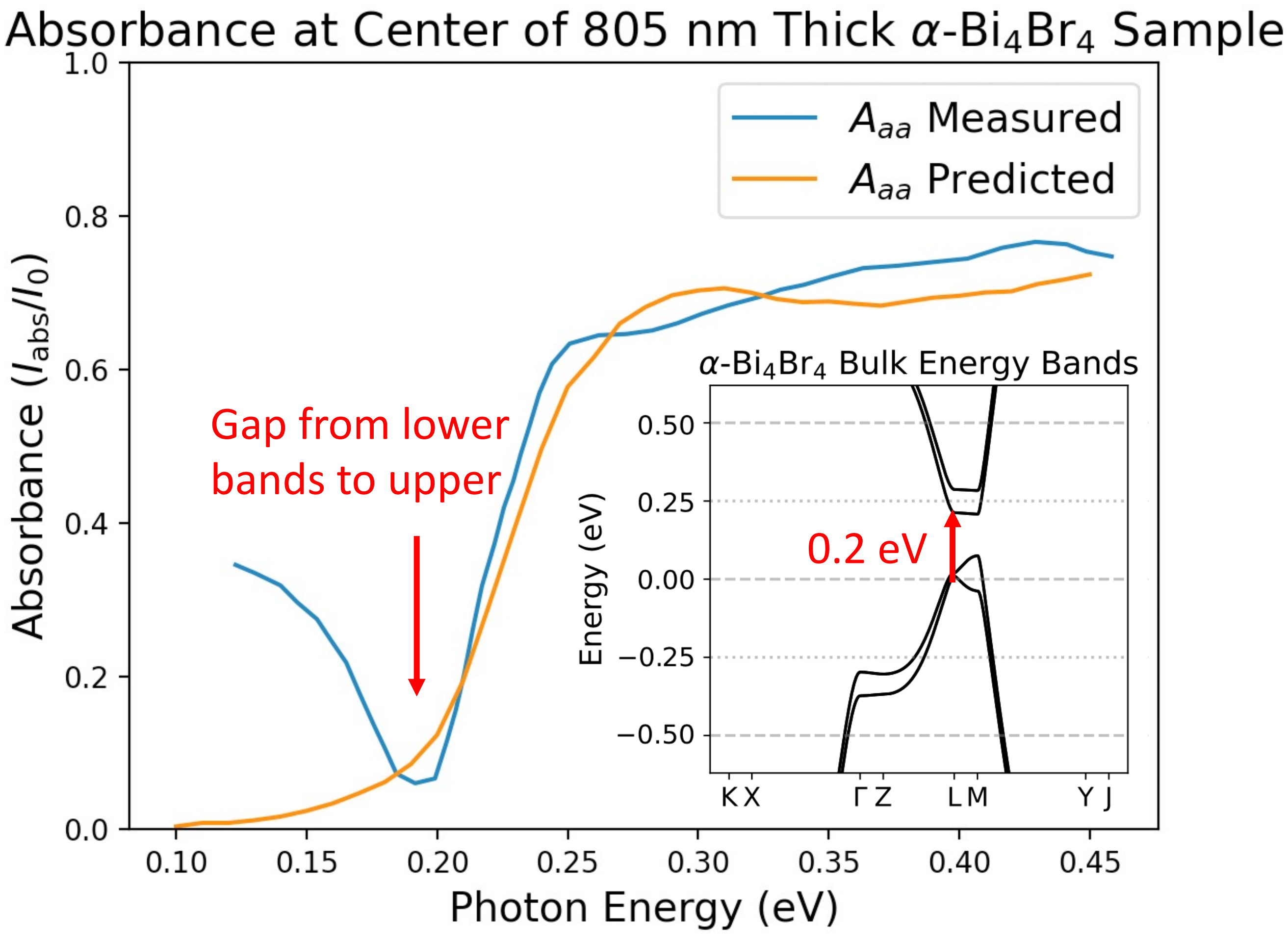
Anisotropic Bulk Response

- Strand direction conductivity dominates over other directions
- Optical conductivity above the band edge is large
- Absorption is about 10^4/cm



Comparison to Experiment

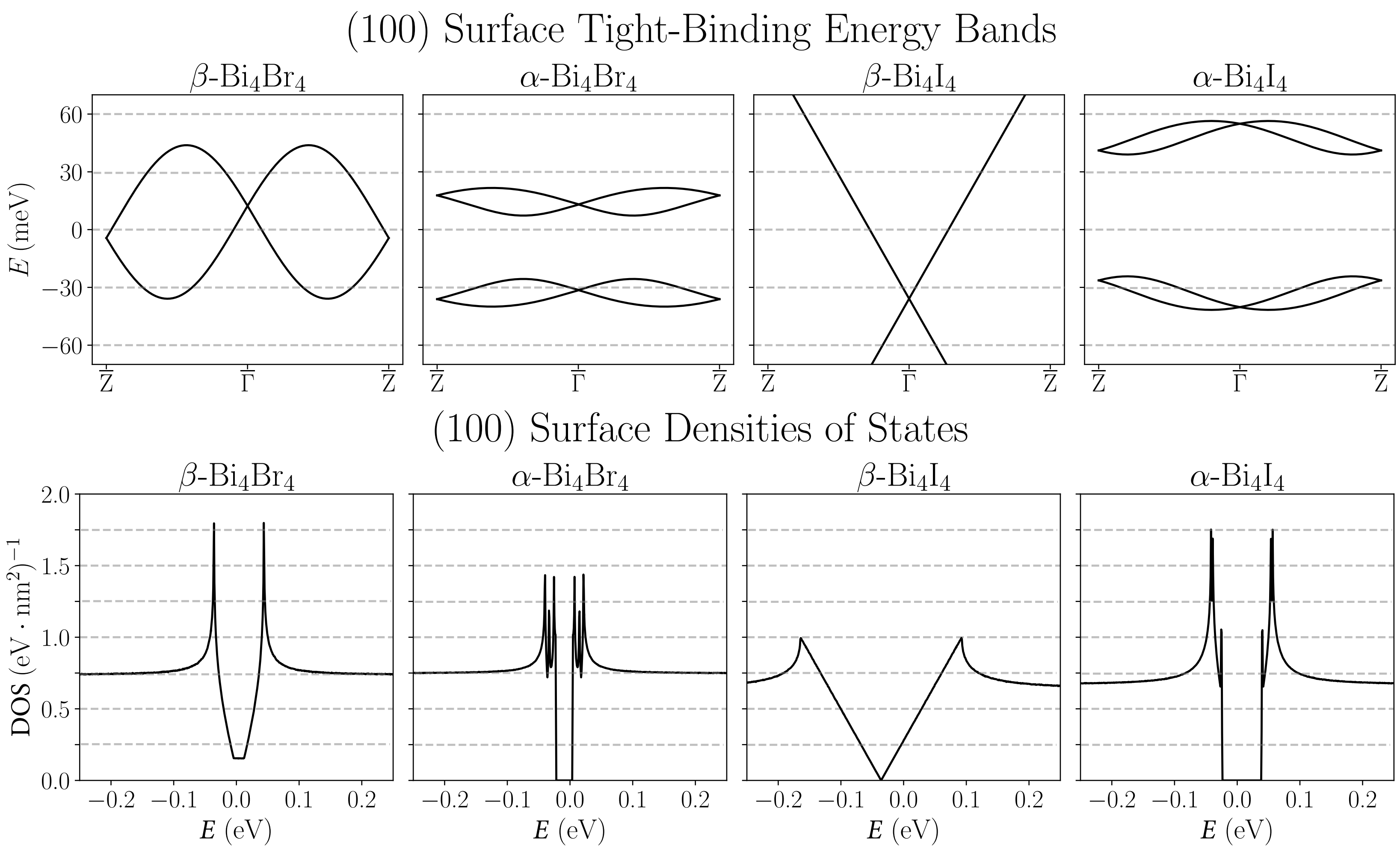
- Experiment
  - Crystals grown on CaF_2 substrate by flux method
  - Linearly polarized light shined on exposed (001) surface
  - Measured absorbance
- Model
  - Fermi energy 137 meV below center of the bulk band gap
  - Beer-Lambert Law
    - $A = (1 - R)(1 - e^{-l\,\mathcal{A}})$



Experimental data from P. Mao, et al. arXiv:2007.00223 (2020).

(100) Surface Band Structure

- Low energy physics happens around q_b=0 since $v_F^b \gg v_F^c$
- Two Dirac cones at different energies (one in STI β-Bi_4I_4)
- α-Bi_4Br_4 exhibits multiple van Hove singularities versus the other structures which only exhibit two



Elliptic Dirac Cone Model

- Universal optical conductance of 2D Dirac Fermions

$$\sigma = \frac{e^2}{4\hbar}$$

- For elliptic Dirac cones this becomes (quick to derive)

$$\sigma_{\mu\mu} = \frac{(v_F^{\mu})^2}{v_F^x v_F^y}\frac{e^2}{4\hbar}$$

- For (100) surface states we have $v_F^b \gg v_F^c$
- Very large (small) and anisotropic response

Optical Absorption of Graphene in the Elliptic Dirac Cone Limit

Let the incident energy flux be (in Gaussian units):

$$W_{\text{incident}} = \frac{\omega^2}{4\pi c}|A|^2 \tag{1.1}$$

And the absorbed power be:

$$W_{\text{absorbed}} = \langle w \rangle \hbar\omega \tag{1.2}$$

Where Fermi's Golden rule gives the transition rate at low temperature ($E_f = \hbar\omega/2$ is the final energy):

$$w = \frac{2\pi}{\hbar}|\langle f|H'|i\rangle|^2 D(E_f) \tag{1.3}$$

Now for graphene in the elliptic Dirac-Cone limit with $\theta = \arg(v_x k_x + i v_y k_y)$:

$$H_0 = \hbar(v_x k_x \sigma_x + v_y k_y \sigma_y) \tag{1.4}$$

$$= \hbar\begin{pmatrix} 0 & v_x k_x - i v_y k_y \\ v_x k_x + i v_y k_y & 0 \end{pmatrix} \tag{1.5}$$

$$= \hbar\sqrt{(v_x k_x)^2 + (v_y k_y)^2}\begin{pmatrix} 0 & e^{-i\theta} \\ e^{i\theta} & 0 \end{pmatrix} \tag{1.6}$$

As above, we consider the perturbations:

$$H'_x = -\frac{e|A|}{\hbar c}\frac{\partial H_0}{\partial k_x} = -\frac{e v_x |A|}{c}\sigma_x \tag{1.7}$$

$$H'_y = -\frac{e|A|}{\hbar c}\frac{\partial H_0}{\partial k_y} = -\frac{e v_y |A|}{c}\sigma_y \tag{1.8}$$

So Fermi's Golden rule gives (for both dir $= x, y$):

$$w_{\text{dir}} = \frac{2\pi}{\hbar}\left(\frac{e v_{\text{dir}}|A|}{c}\right)^2 \frac{2\sin^2(\theta) + 2\cos^2(\theta)}{4} D(E_f) = \frac{\pi}{\hbar}\left(\frac{e v_{\text{dir}}|A|}{c}\right)^2 D(E_f) = \langle w_{\text{dir}} \rangle \tag{1.9}$$

The number of states per volume is (with $E = \hbar\sqrt{(v_x k_x)^2 + (v_y k_y)^2}$) (recall the area of ellipse is $\pi r_1 r_2$):

$$\frac{N}{V} = \frac{\pi k_x^{\max} k_y^{\max}}{(2\pi)^2} = \frac{\pi E^2}{(2\pi)^2 \hbar v_x v_y} \tag{1.10}$$

So the density of states is (with $E_f = \hbar\omega/2$):

$$D(E_f) = \frac{\hbar\omega}{4\pi\hbar^2 v_x v_y} \tag{1.11}$$

So, we see that the absorption is:

$$P_{\text{dir}}(\omega) = \frac{\langle w \rangle \hbar\omega}{W_{\text{incident}}} \tag{1.12}$$

$$= \hbar\omega\frac{\pi}{\hbar}\left(\frac{e v_{\text{dir}}|A|}{c}\right)^2 \frac{\hbar\omega}{4\pi\hbar^2 v_x v_y}\frac{4\pi c}{\omega^2|A|^2} \tag{1.13}$$

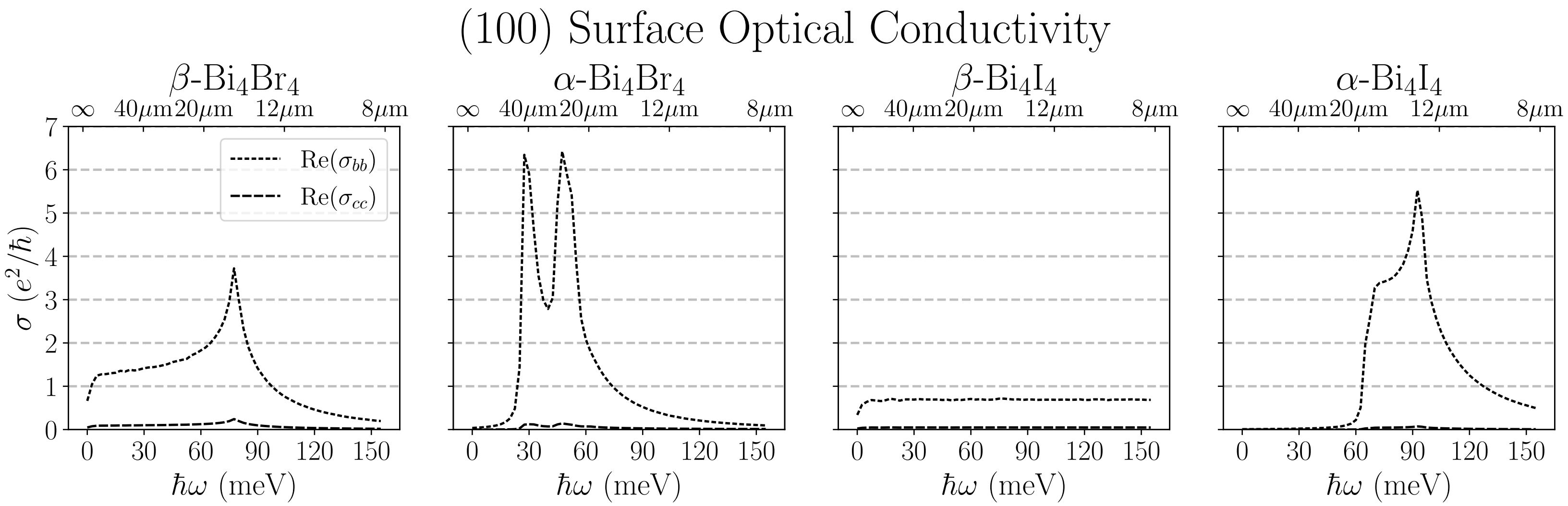
$$= \frac{\pi e^2}{\hbar c}\frac{v_{\text{dir}}^2}{v_x v_y} \tag{1.14}$$

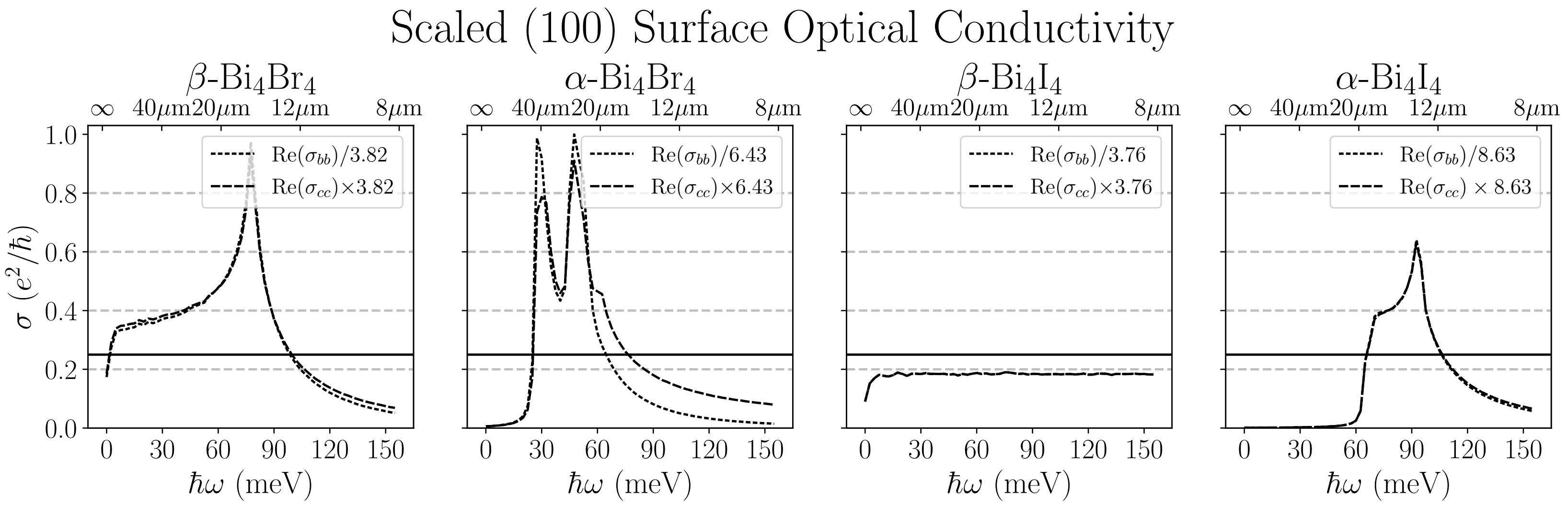
$$= \pi\alpha\frac{v_{\text{dir}}^2}{v_x v_y} \tag{1.15}$$

Which is $\pi\alpha$ when $v_x = v_y$.

Anisotropic (100) Surface Response

- Optical conductivities are qualitatively like the Dirac conductivity of graphene
  - Except α-Bi_4Br_4
    - Different JDOS
- Strand direction conductivity dominates transverse conductivity
- Directions are almost related by a scalar multiple (elliptic Dirac)

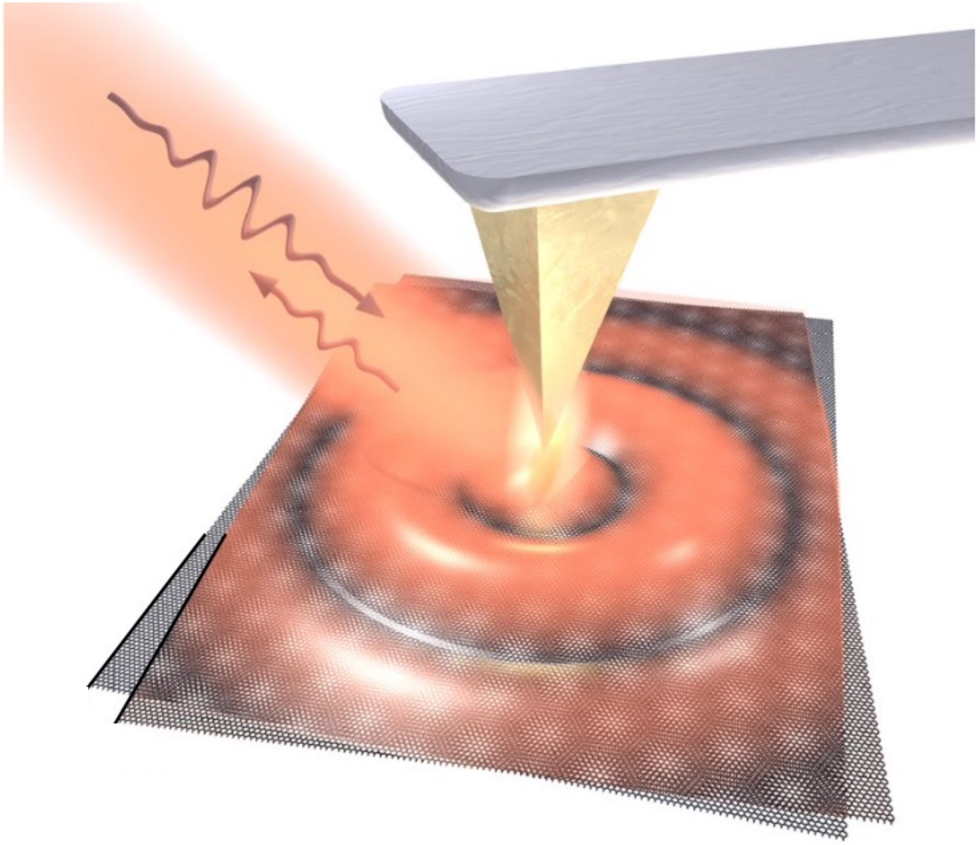




Surface Plasmon Polaritons (SPPs)

- Plasmon polaritons are near-field quasiparticles that form in materials with negative permittivities
- 3D plasmons are forbidden in Bi_4X_4 since the imaginary part of the optical conductivity is never positive, so the real part of the permittivity is never negative
- Plasmons are described by a quality factor

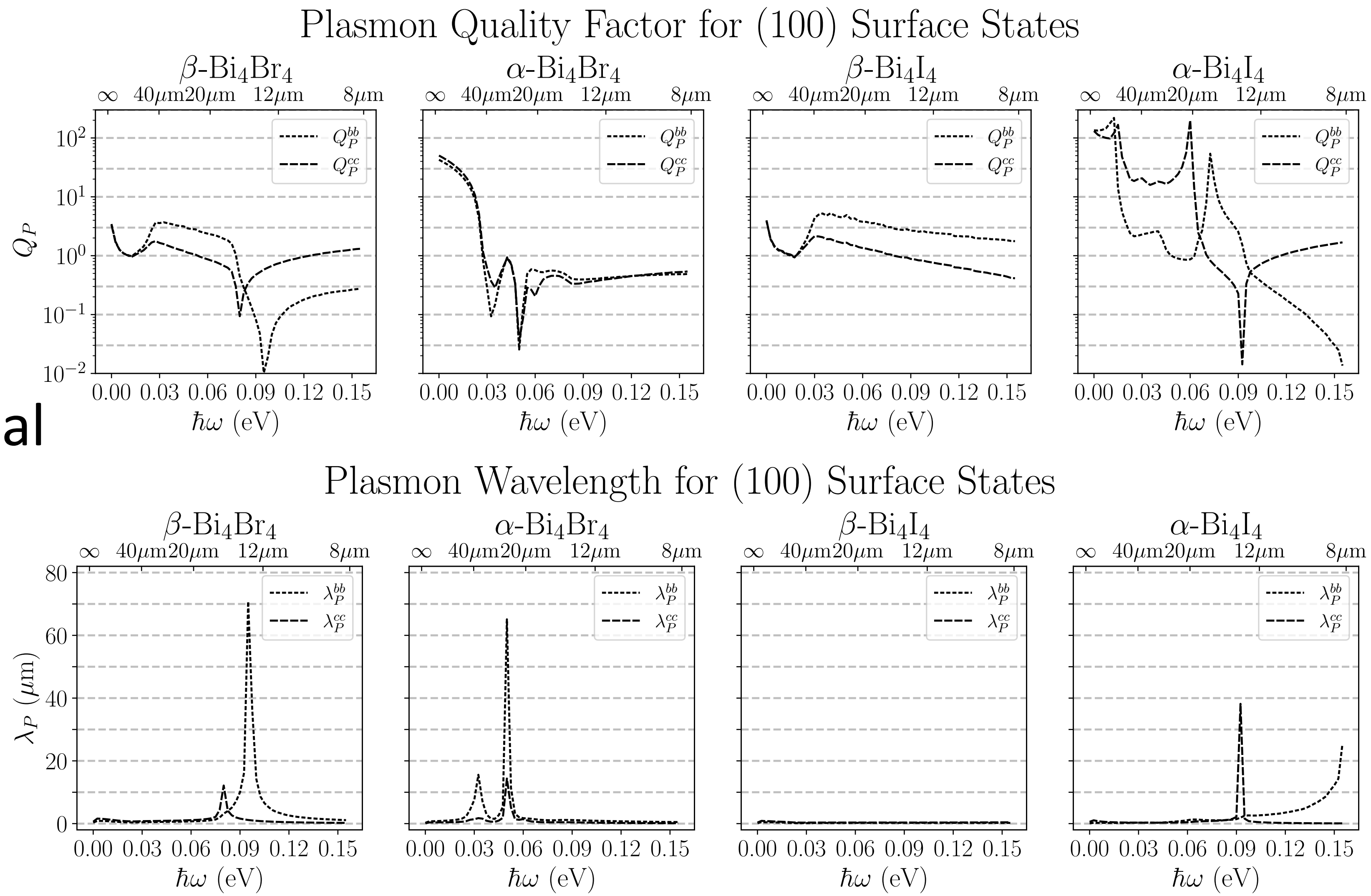
$$Q_P = \frac{\mathrm{Im}(\sigma)}{\mathrm{Re}(\sigma)}$$



1. N. Hesp, et al. Nat. Phys. **17**, 1161 (2021)

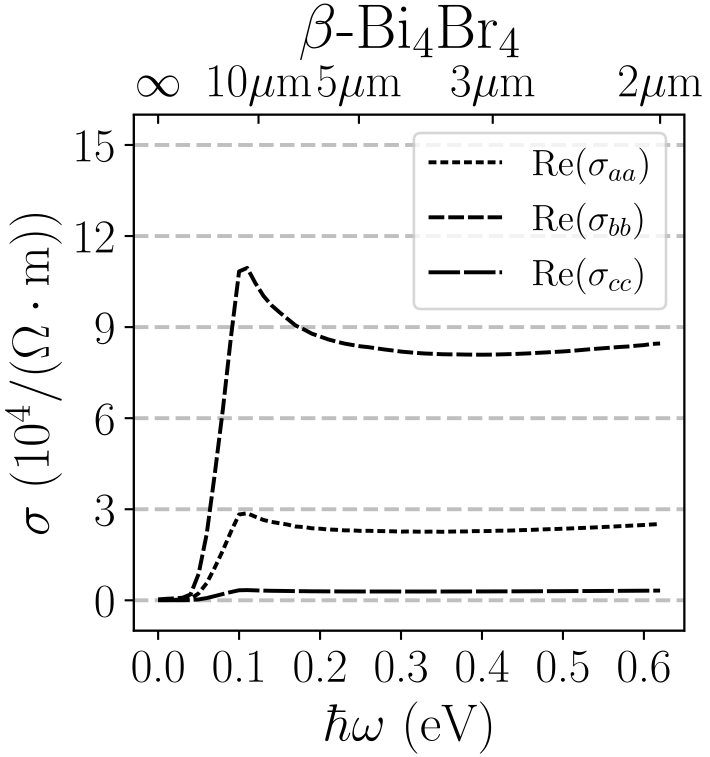
Anisotropic SPPs from (100) Surface States

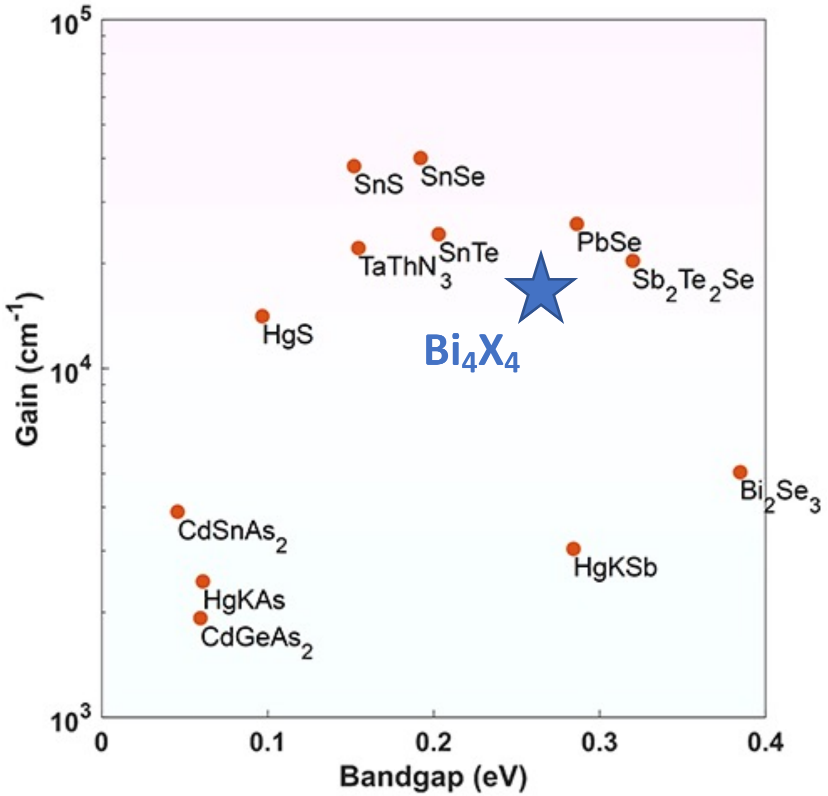
- Q_P for plasmons in the strand direction and the perpendicular direction can be very different, corresponding to the anisotropy of the material
- This may lead to the formation of quasi-1D SPPs that decay more quickly in one direction than the other



Result 1: Large and Anisotropic Bulk Response

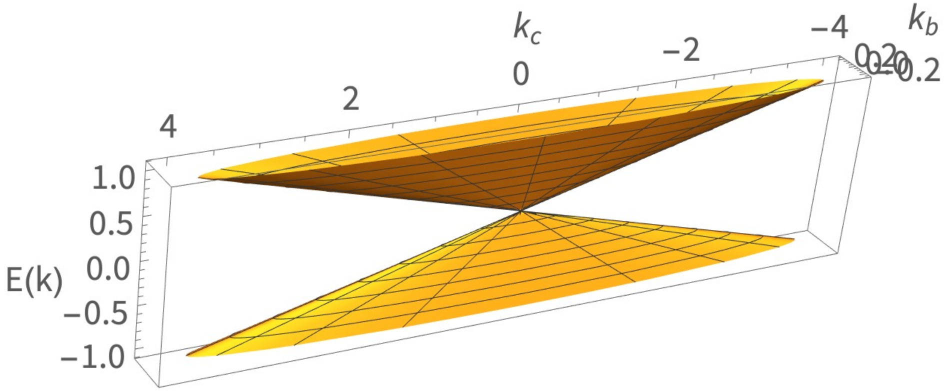
- Optical conductivity and gain surpass conventional HgCdTe photodiodes by an order of magnitude
- Compared to other materials with similar band inversions the response is anisotropic
    - Speculative possibility for polarization-dependent charge coupled photodiodes

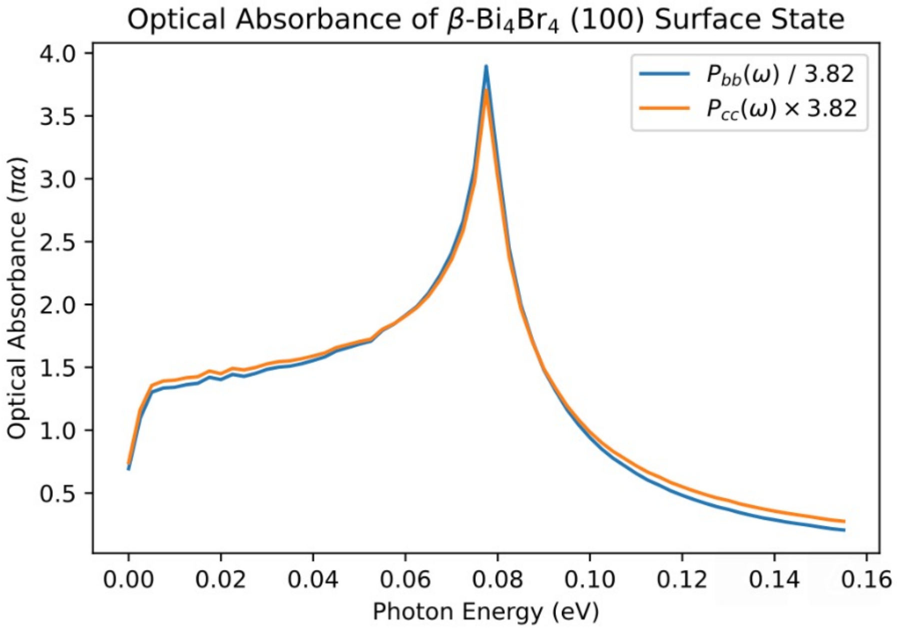




Result 2: Signatures of Elliptic Dirac Cones

- Side surfaces are TIs with one (strong) or two (weak) Dirac cones
- This leads to characteristic conductance and absorbance features
- These materials are quasi-1D
- Conductance features are anisotropic
  - Enhanced in strand direction
  - Suppressed perpendicular to it





Result 3: Quasi-1D Surface Plasmon Polaritons

- SPPs have been proposed as a platform for room-temperature quantum emitters[1]
- Speculatively, quasi-1D SPPs on the (100) surfaces of Bi_4X_4 may provide an avenue for highly polarized quantum emitters[2]

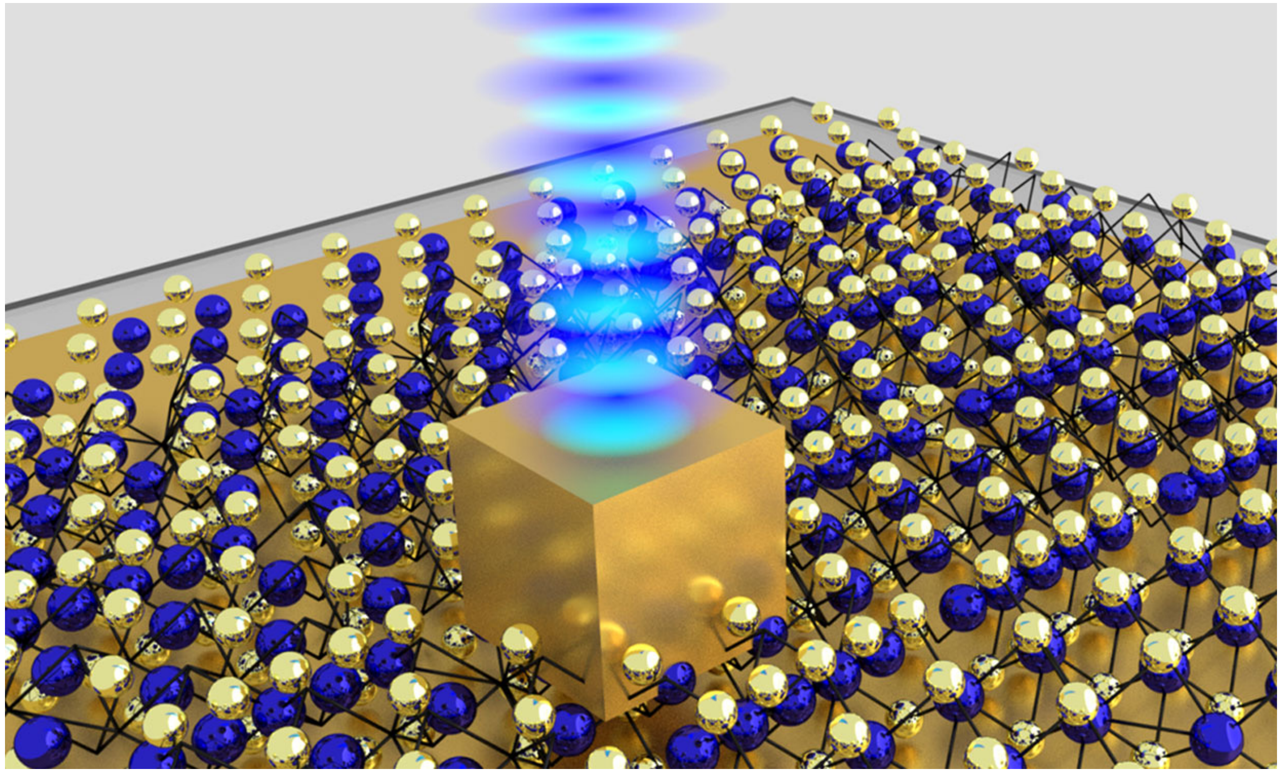


Image from IEEE Spectrum

1. T. Hoang, et al. Nano. Lett. **16**, 270 (2016)
2. Q. Wang, et al. Nano. Lett. **21**, 7175 (2020)

Outlook

- Quasi-1D materials, as exemplified by Bi_4X_4 exhibit a rich and unusual set of electronic states and properties
- Real space, momentum space, and transport studies of these materials have elucidated the properties of these materials
- A speculative frontier for $Bi4X_4$ in optoelectronics
  - Polarized large gain charge coupled diodes
  - Polarized quantum emitters

Acknowledgements

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