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Studying Stoichiometric Variation's Influence on Photoemissive Properties of Cs-Sb Films Using DFT and Monte Carlo Simulations

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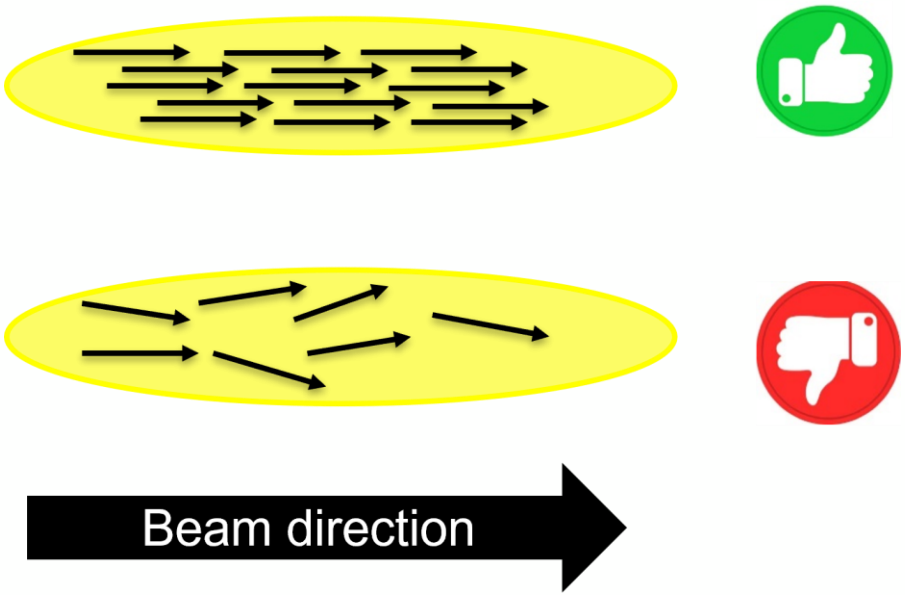
Motivation

- Alkali antimonide thin-film photocathodes are known candidates for high quality, bright electron beam sources
- Scattering mechanisms in the transport phase and stoichiometry are known to influence photoemission, but the exact governance is not well-understood
- Density Functional Theory (DFT) and Monte Carlo simulations can be combined to study both phenomena in detail [1]
- **Objective 1:** Develop photocathodes for high peak-intensity beam generation with < 10 meV Mean Transverse Energy (MTE) and good quantum efficiency (QE)
  - **Deliverable 1.3:** First principles predictions of MTE and QE spectral response for relevant photocathode materials (Fall 2026)
- **Objective 2:** Design materials for long-lived cathodes in extreme electric field and high average current
  - **Deliverable 2.2:** Photocathode that can operate for >1 week with MTE <100 meV and QE>1% under high average current (>50 mA) conditions (Summer 2026)

[1] O. Chubenko, *et al*., J. Appl. Phys. **130**, 063101 (2021).

Brightness

- Beam brightness is dictated by the quality of the photocathode
- Brightness is primarily determined by the MTE and QE
- Bright beams are essential to advanced accelerator applications because they provide an increased resolution and are much more spatially and temporally precise



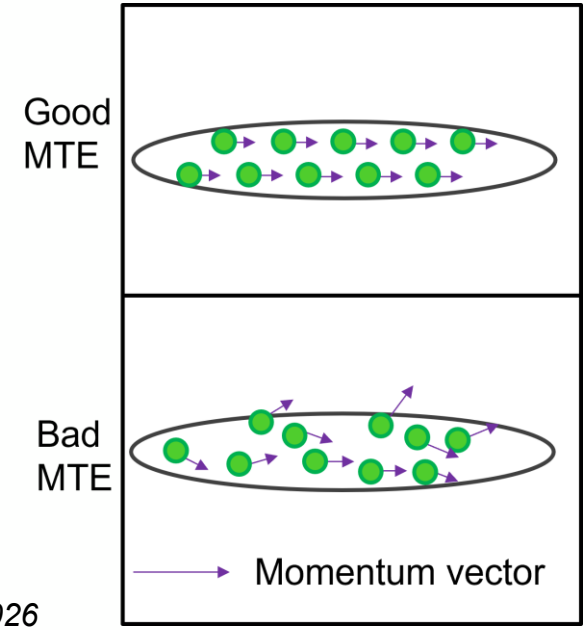
$$B_{4D} \propto \frac{(E_z)^k}{MTE}$$

(High charge density regime)

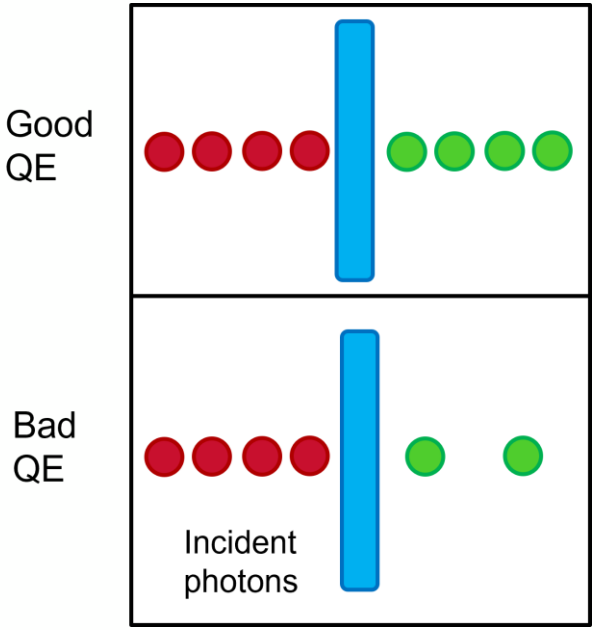
MTE and QE

- MTE and QE are the primary measures of an electron source's quality
- They are dictated by crystalline properties and stoichiometry
  - Electronic band structure (band gap, effective mass, etc.)
  - Surface effects influence emission threshold
  - Optical properties are closely related to photoemission since they dictate how the crystal interacts with light

$$MTE = \frac{m\langle v_\perp \rangle^2}{2}$$

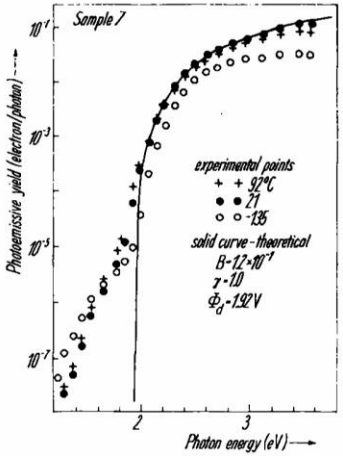


$$QE = \frac{\#\ of\ emitted\ electrons}{\#\ of\ incident\ photons}$$

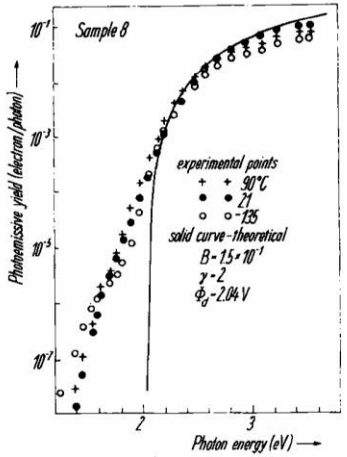


Stoichiometry

- In this presentation, stoichiometry has two meanings:
  - The primary crystals we are currently interested in are Cs_3Sb and CsSb. These are two different crystals entirely and therefore two different stoichiometries
  - There is also stoichiometric variation. The stoichiometry of Cs_3Sb is varied such that it becomes $Cs_{3-x}Sb$ where x is the variation ($|x|<1$). Under this condition, this crystal still resembles Cs_3Sb
    - The variation x can be positive or negative depending on if the crystal is Cs-deficient or Cs-rich. For this talk, only Cs-deficient ($x>0$) is of interest
- Stoichiometry is known to influence photoemission in semiconductors, particularly in Cs_3Sb [2,3]

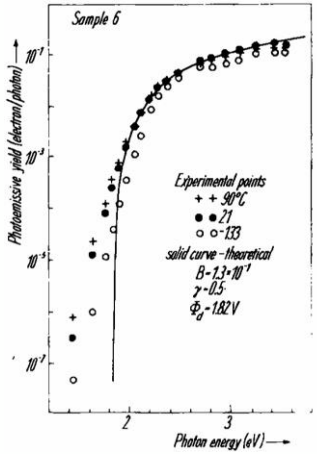


Near Cs_3Sb

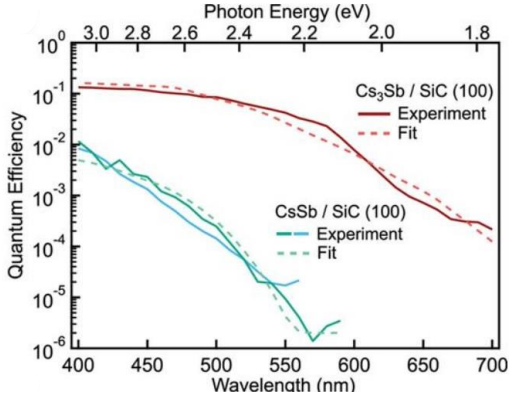


Cs-rich

[3]



Sample with high yield

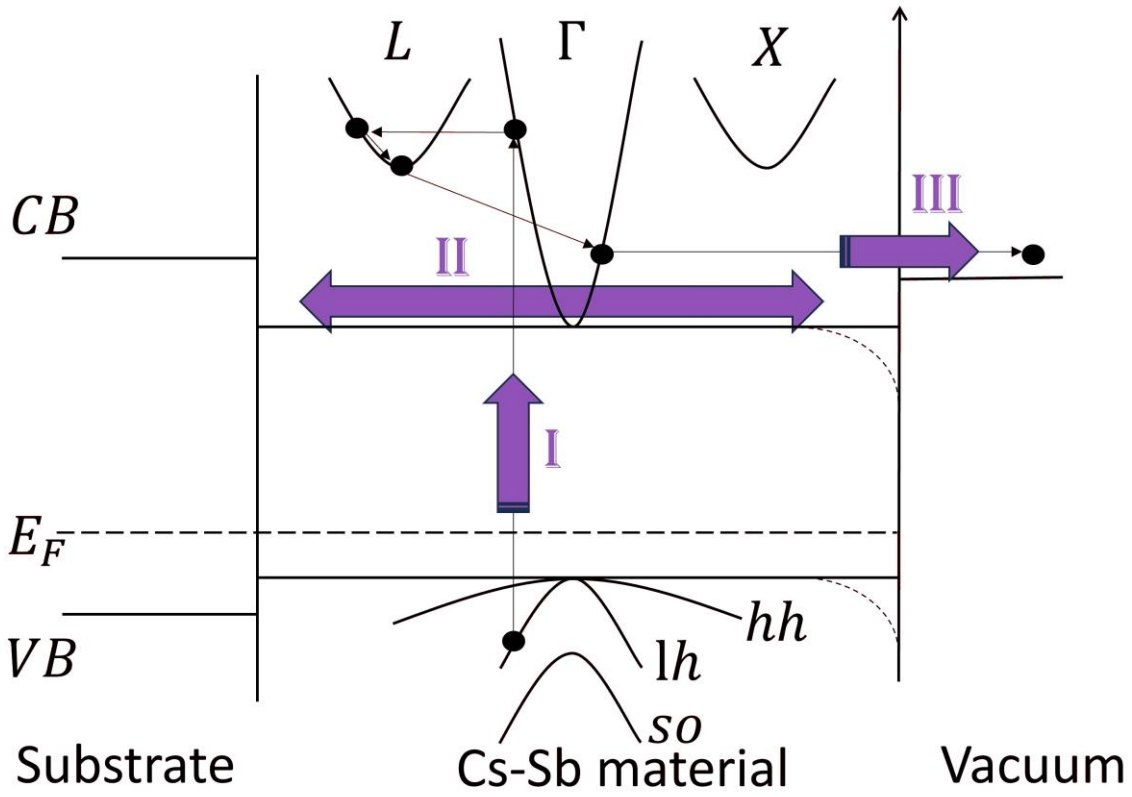


[4]

[2] V. Pavlenko, *et al.*, Appl. Phys. Lett. **120**, 091901 (2022).
[3] Hagino et al, Phys. Stat. Sol. **17**, 609 (1966).
[4] Parzyck et al., APL Mater. **11**, 101125 (2023)

Monte Carlo

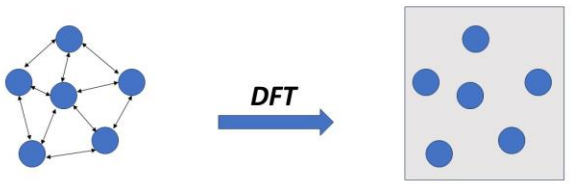
- Three Step Model
  - **I**-photoexcitation of electrons from the Valence Band (VB) to the Conduction Band (CB)
  - **II**-transport of electrons to the surface
  - **III**-emission into the vacuum



DFT

- Concept
  - Reduce the many body system to a Kohn-Sham system with the same non-interacting density as the interacting system
  - Solve the resulting Hamiltonian to find the most likely eigenstates and their eigen energies (ie the energy of the electrons)

$$E\Psi = \sum_{i=1}^{N} \frac{-\hbar^2}{2m_i} \nabla^2 \Psi + \sum_{i=1}^{N} V(\boldsymbol{r}_i)\Psi + \sum_{i<j}^{N} U(\boldsymbol{r}_i, \boldsymbol{r}_j)\Psi \rightarrow \sum_{j} U(\boldsymbol{r}_i, \boldsymbol{r}_j)$$

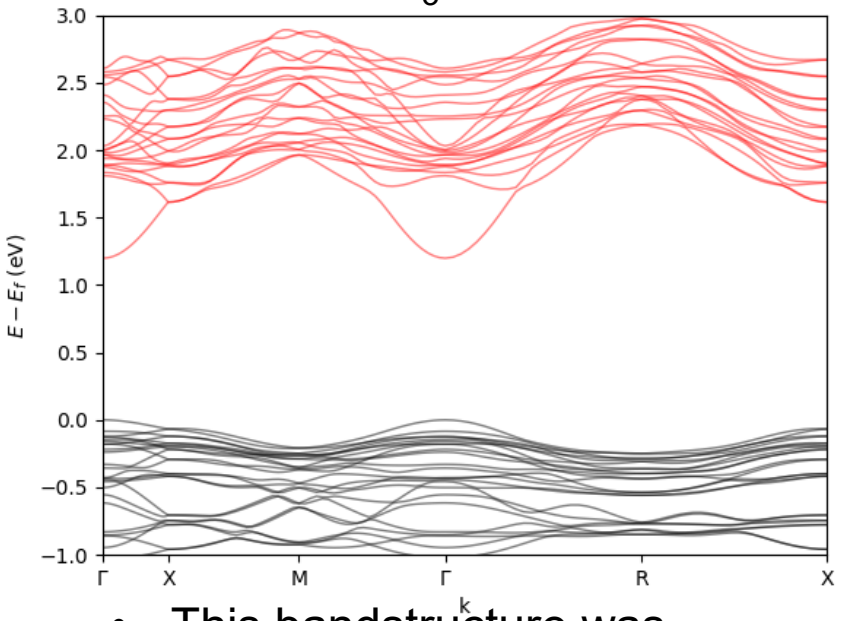


$$U_{eff}$$

Preliminary Results

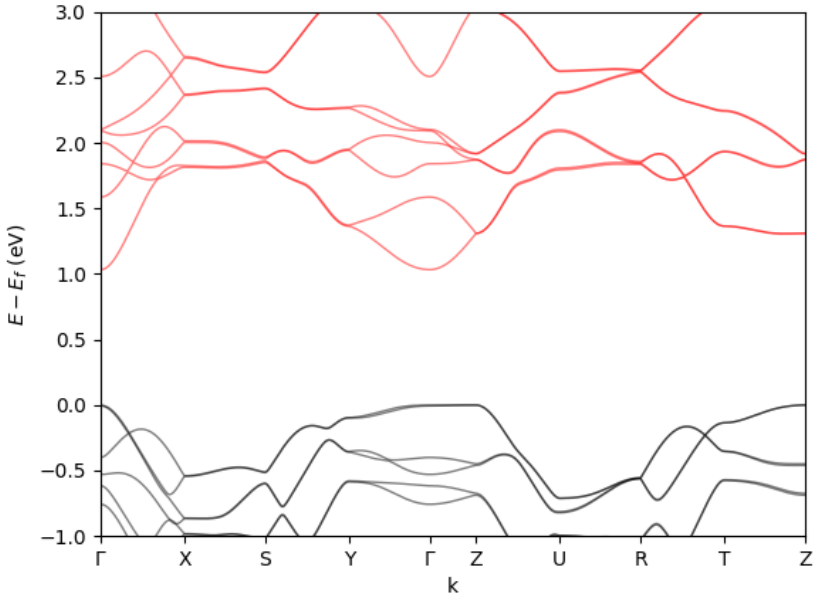
- Bandstructures for Cs_3Sb and CsSb

Cs_3Sb



- This bandstructure was calculated using DFT+U to correct for DFT's known underestimation of bandgaps.
- U = 1.7 eV applied to Sb 5-P orbital
- BG = 1.1987 eV

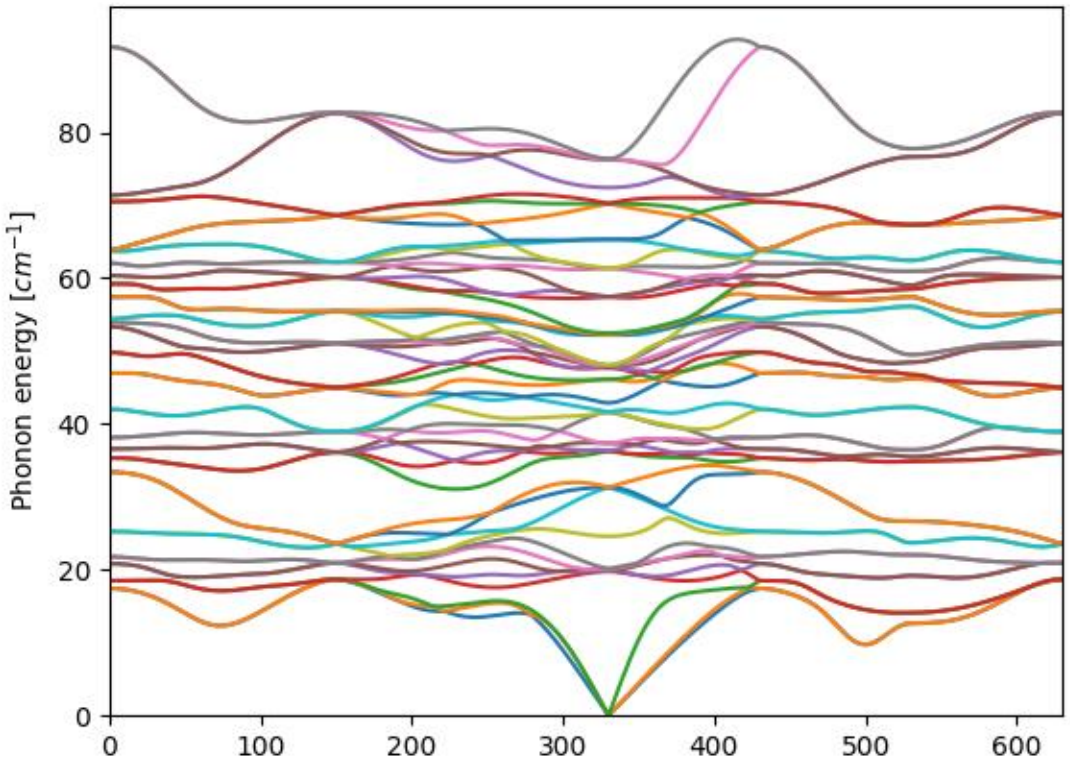
CsSb



- This bandstructure also comes from DFT+U. The value of U is used in the same manner as Cs_3Sb
- BG = 1.0324 eV
- The bandgap and use of U is going to be discussed shortly

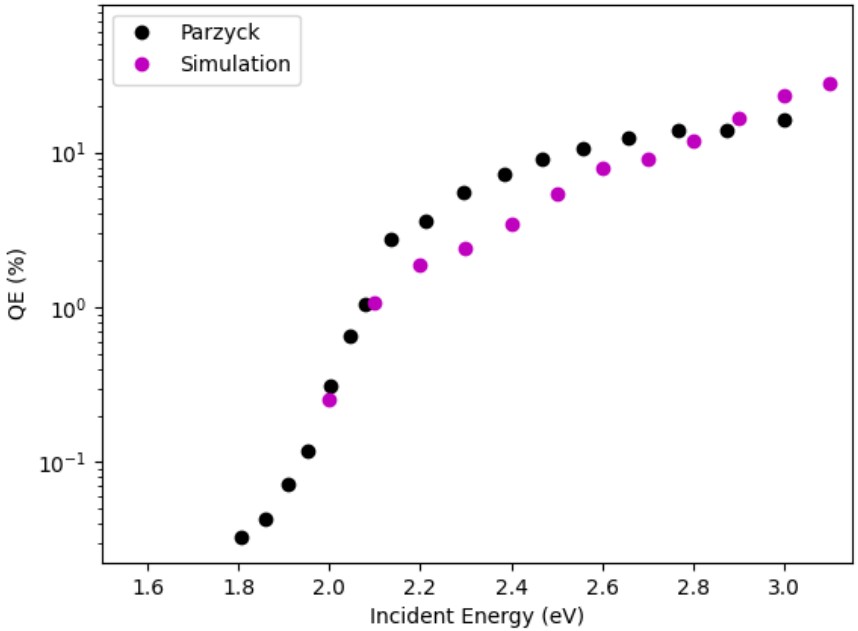
Preliminary Results

- Phonon dispersion for Cs_3Sb
  - Calculations for CsSb are undergoing

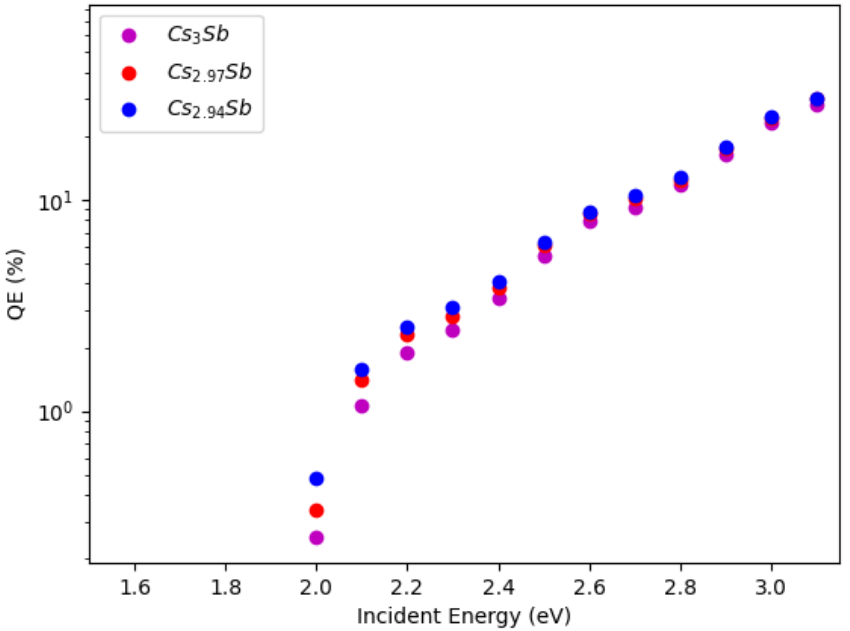


Preliminary Results

- Comparison of calculated QE to experimental data [4] and stoichiometry's calculated influence on QE



Stoichiometric Cs_3Sb

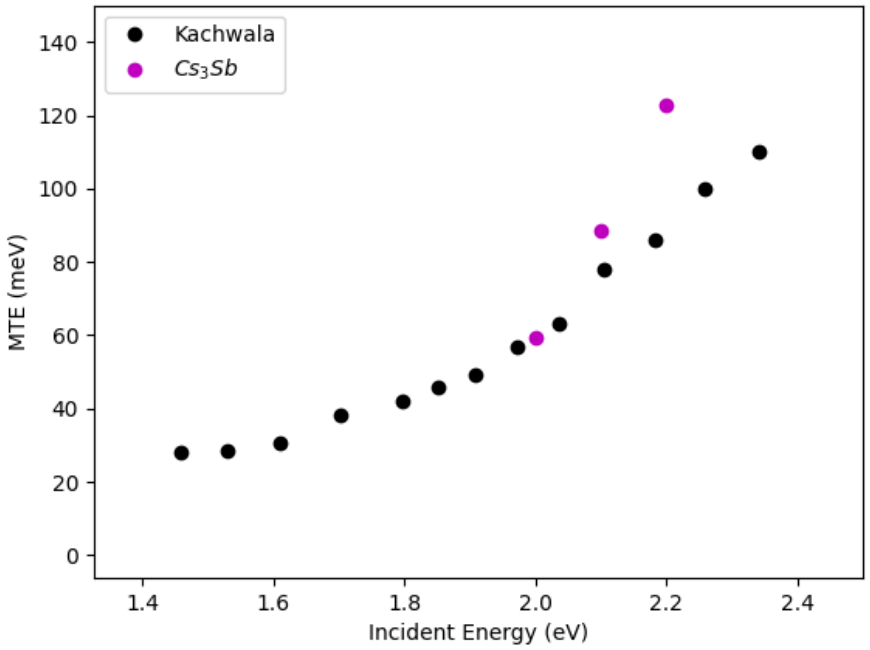


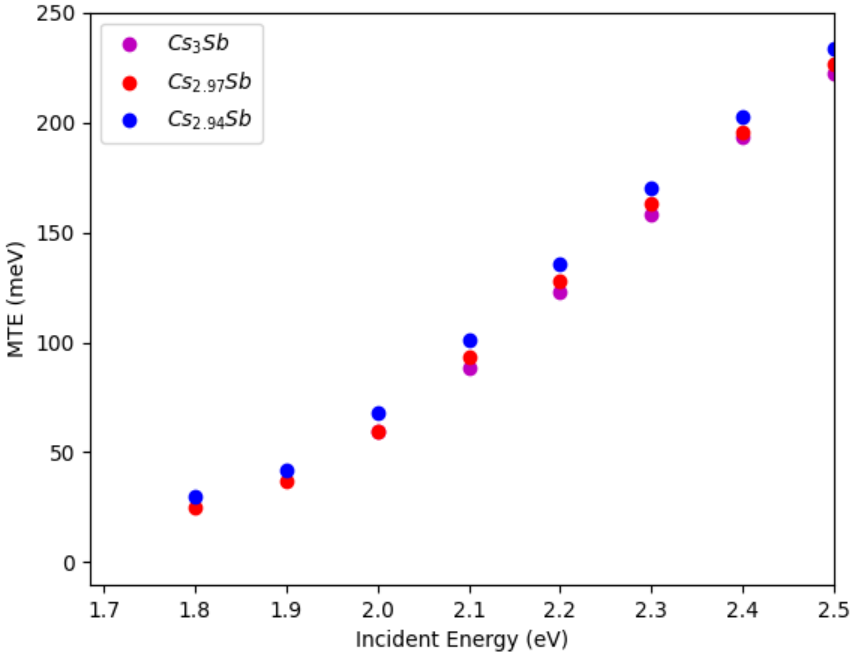
Varying $Cs_{3-x}Sb$

[4] Parzyck et al., APL Mater. **11**, 101125 (2023)

Preliminary Results

- Comparison of calculated MTE to experimental data [5] and stoichiometry's calculated influence on MTE





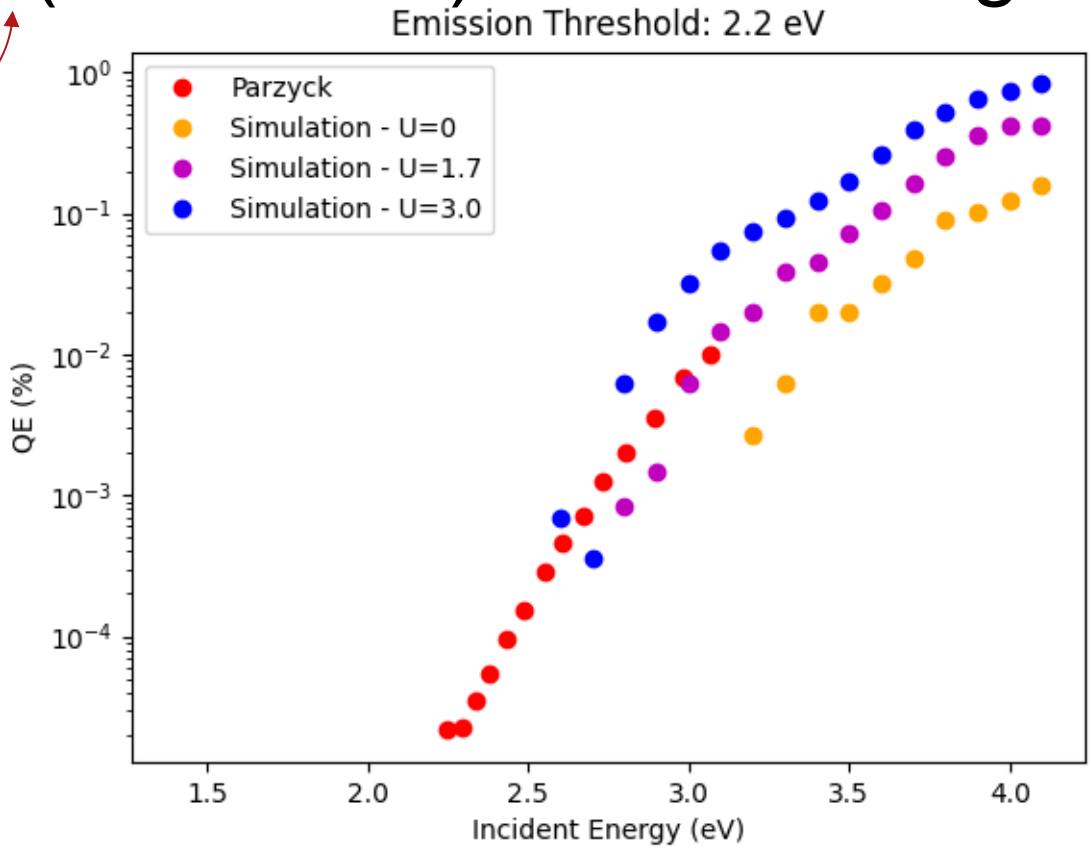
Stoichiometric Cs_3Sb

[5] A. Kachwala, *et al.*, Appl. Phys. Lett. **123**, 044106 (2023).

Preliminary Results

- CsSb has a reported bandgap of 0.56 eV which our PBE (basic DFT) calculation agrees with

Ya basic! DFT+U can (and does!) provide more accurate bandgaps



By assuming an emission threshold using experimental data, define Ea = ET – BG where Ea is electron affinity, ET is emission threshold, and BG is the calculated bandgap. This allows us to check bandgaps by comparison of QE against a crystal with the exact same emission threshold

Future Work

- Finalize table of parameters from DFT for Cs_3Sb and CsSb using DFT+U
- This process is *ab initio* and therefore will work with any crystal. It is intended to apply this process to various crystals such as Cs_2Te and other more exotic stoichiometries of cesium antimonide
- There is far-off interest in utilizing machine learning to search for photocathode candidates

Conclusion

- DFT and Monte Carlo was used to calculate with reasonable agreement QE and MTE
- Stoichiometric variation was successfully implemented in the model and it was shown that it does not hinder the model's performance
- It was verified computationally that Cs-deficient Cs_3Sb has a slightly increased QE and lowered emission threshold, as expected
  - All arguments for this in literature were supported with experimental data

Acknowledgements

- This work was supported by the U.S. National Science Foundation under Award PHY-1549132, the Center for Bright Beams.
- This work was supported by the DOE under the SCGSR award, 2024 Solicitation 2
- Thank you to Tyler Wu, Kevin Nangoi, and Prof. Tomas Arias from Cornell University for continuous guidance in working with JDFTx/DFT.
- Thank you to Enrique Batista and Sandip Aryal (LANL) for further DFT resources and to Vitaly Pavlenko for hosting me at LANL
- This work used resources of the Center for Research Computing and Data at Northern Illinois University.

- Programs Used

- Direct Calculation: Quantum Espresso ran on the incomparable NIU METIS cluster, Monte Carlo model developed by Prof. Oksana Chubenko
- Postprocessing: Mathematica, Python