Computational Methods for Cathode Design

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LAPPD2 Theory-Based Photocathode Godparent Review
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Argonne-IIT-PNNL Photocathode Collaboration

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Outline

Motivation – approach	K. Harkay
Detailed computations amd results	K. Németh

Introduction

- Ultra-bright photocathodes are a key technology for the development of future accelerator-based light sources.
- Two development approaches are applicable, depending on time-frame:
  - **Near-term**: Optimize the synthesis and performance of long-known photocathodes such as Cs_2Te, CsKSb, GaAs (ANL, ASTeC, BNL, HFZD, INFN, JLab, LBNL, PITZ, et al.)*
  - **Mid-to-far-term**: Explore novel crystal systems numerically and optimize ("design") their properties, or nano-engineer surfaces, or other novel idea (**ANL**, ASTeC, BNL, Eindhoven, Jlab, LBNL, SLAC, UCLA, Vanderbilt, et al.)*
- Properties to design or tune include:
  - Intrinisic emittance, Workfunction, QE
  - Reliability, robustness (vacuum, E-field, field emission)

* Accelerator community; D. Dowell et al, NIM A 622, 685 (2010).

Designer cathode development

Design *(accelerator & condensed matter physics, computational chemistry)*

- Derive cathode requirements from future light source requirements.
- Investigate candidate systems; think "outside the box," borrow ideas from other fields (e.g., surface catalysis).
- Compute electronic properties.
- Select systems with promising predicted properties for synthesis.

Synthesize *(chemistry, materials science)*

- Develop & test hypotheses for chemical reactions.

Characterize *(surface science, materials science)*

- Compare measurements with predictions, using all available diagnostics.
- For air-sensitive cathodes: Develop portable load-lock system and cross-compatible sample transfer system.

Computational approaches

- Mostly focused on Spicer's photoemission 3-step model (photon absorption, electron transport, electron emission). Each approach has advantages and limits:
  1. Density Functional Theory (DFT) modeling to compute photoelectron dynamics from quantum mechanical wave function of the system (K. Németh et al). Addresses steps 1 & 3 of 3-step model.
  2. Particle-in-cell (PIC) photoemission modeling, e.g. VORPAL (D. Dimitrov, TechX); includes electron transport. Needs input parameters (dielectric constant, etc), possibly from DFT.
  3. Monte Carlo simulations using parametrized scattering probabilities; diffusion + drift-plasma models (Z. Insepov, K. Attenkofer et al).
  4. Genetic multivariate optimization -- used in
     a) Accelerator optics design (APS, Cornell, etc)
     b) Cascade laser bandstructure design (Ines Montano, Sandia)
- It may be an advantage to combine the approaches, or to develop a 1-step model in the future.

Our design approach

Main tool:

- Quantum-chemical Density Functional Theory (DFT)-based surface-physics calculations.

Two codes used:

- PWSCF (crystal lattice parameters, workfunction, gap energy, surface energy, density of states)
- YAMBO (optical absorption spectra)

Three of our cathode concepts:

- Tuning workfunction and intrinsic emittance using ultrathin films.
- Tuning the workfunction of Cs_2Te: Cs_2TeC_2 and Cs_2Te_5.

Chemically Inert Low Workfunction Surfaces from Ultrathin Oxides on Metal Substrates

TABLE 1. Work Functions (Φ) of Metal and Oxide Thin Films on Metals from DFT Calculations

	Φ_m, eV	$\Phi_{m/d}$, eV
FeO/Pt(111)	5.8	5.8–6.4
TiO_2/Pt(111)	5.8	5.6
$SiO_{2.5}$/Mo(112)	4.2	4.9
NiO/Ag(100)	4.3	3.9
MgO/Ag(100)	4.3	3.0
BaO/Au(100)	5.1	2.3
MgO/Mo(100)	4.2	2.1
BaO/Ag(100)	4.3	2.0
BaO/Pd(100)	5.2	2.0

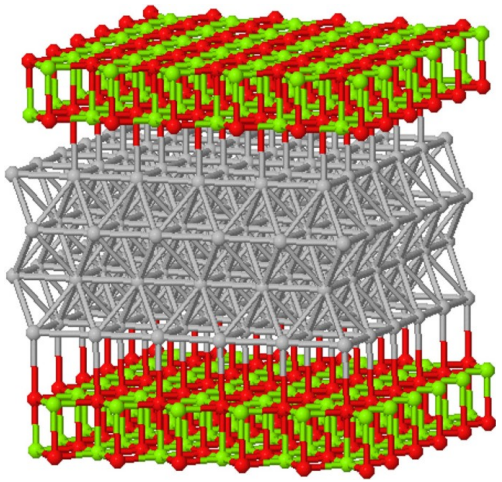
Giordano and Pacchioni, Accounts of Chemical Research **44**, 1244 (2011)

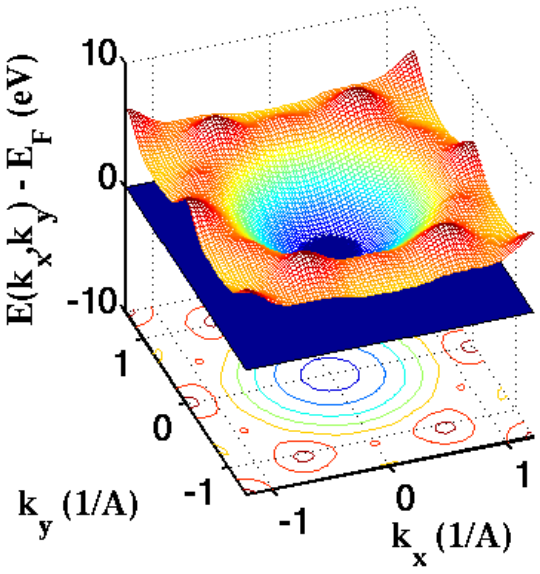
Examples of Validation of Workfunction Calculations

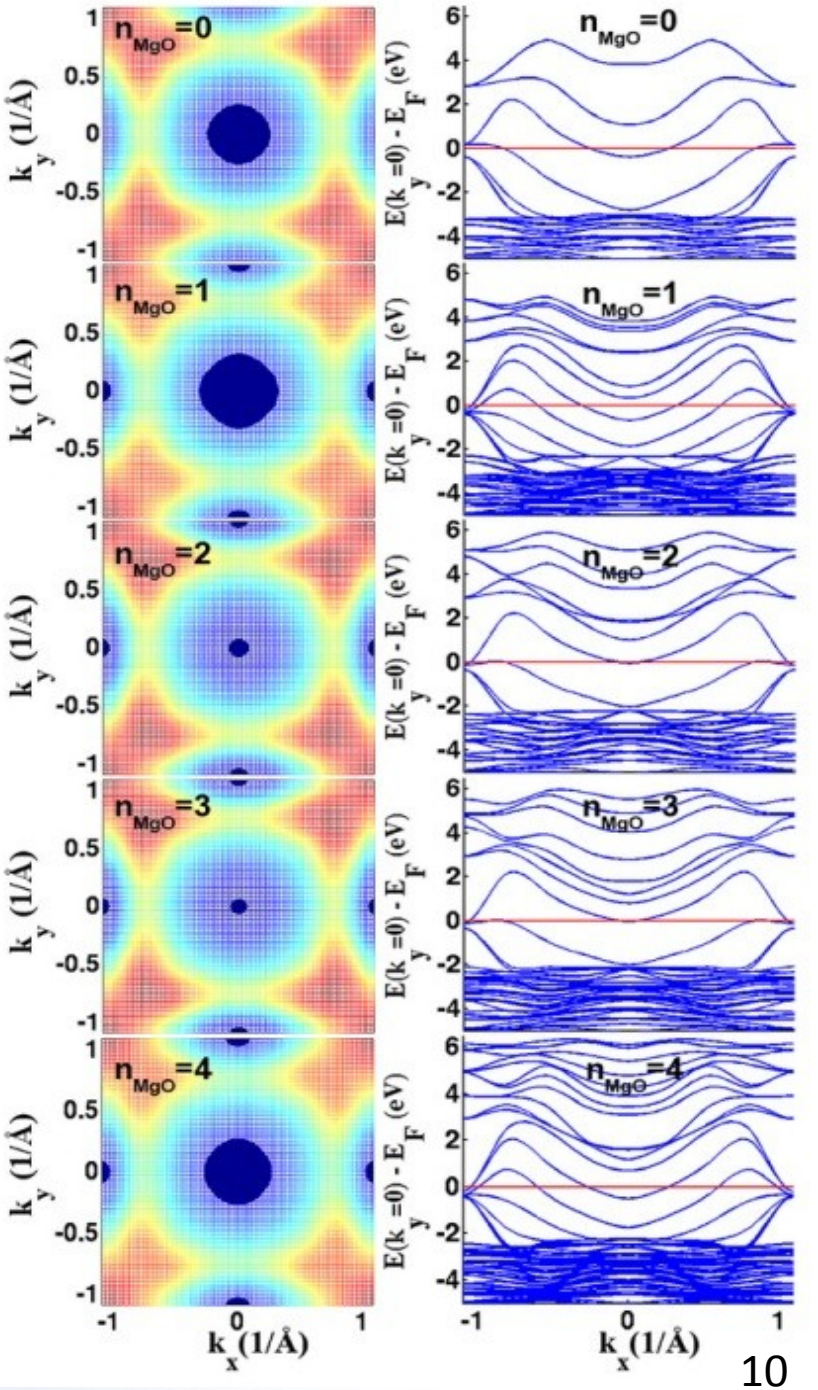
TABLE III. Experimental and calculated (DFT) properties of photoemissive surfaces of validation materials: Work functions (Φ), band gaps at the Γ-point $E_g(\Gamma)$, and surface energies (σ).

Compound surface	Φ (eV)		$E_g(\Gamma)$ (eV)	σ (eV/Å^2)
	Expt.	DFT	DFT	DFT
Cs(100)	2.14[21]	2.00	0.29	0.005
Te(001)	4.95[21]	5.02	0.54	0.036
Cs_2Te(001)	2.90–3.0[22]	3.08	0.77	0.015
Cs_2Te(010)	2.90–3.0[22]	2.90	1.04	0.014
(Cs)Na_3KSb	1.55[23]	–	–	–
K_2CsSb	1.9–2.1[24,25]	–	–	–

MgO:Ag(001)







1. The workfunction reduces from 4.3 eV to 3.0 eV due to MgO thin layers.

2. The surface parallel crystal momentum, $\hbar k_x$, is preserved in photoemission → → angle of photoemission cone.

K. Nemeth, K. C. Harkay et al.
PRL 104, 046801 (2010)

Chemical Redesign of Cs_2Te: Acetylation Leads to 2.4 eV Workfunction with High QE

Motivation: turn Cs_2Te into a visible-light photocathode with preserved QE.

Design idea: incorporate an easy to excite pi-electron system into Cs_2Te .

J.Z. Terdik, K. Nemeth, K.C. Harkay et al., PRB, 86, 035142 (2012).

$$Cs_2Te(cr) + C_2H_2(g) \rightarrow Cs_2TeC_2(cr) + H_2(g)$$

$$Cs_2C_2(cr) + Te(cr) \rightarrow Cs_2TeC_2(cr)$$

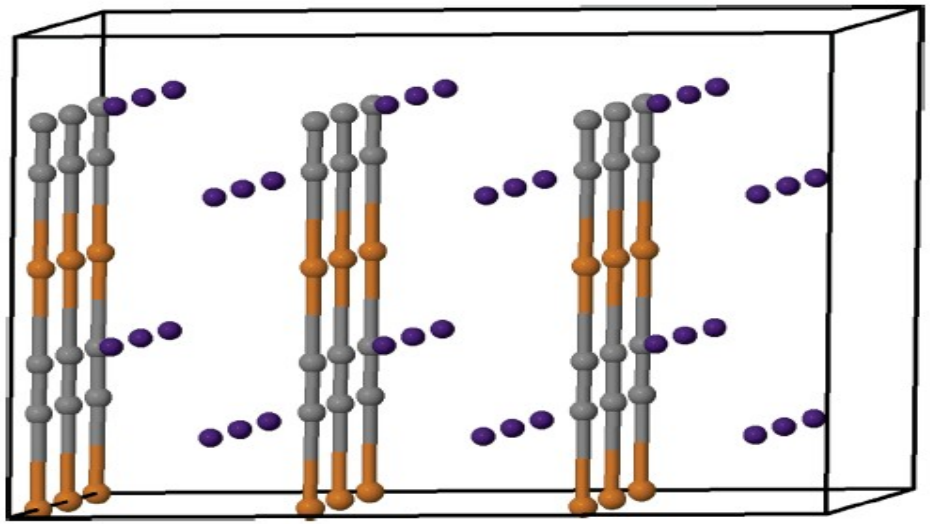


FIG. 1. (Color online) A side view of the 3 × 3 × 2 supercell of the hexagonal unit cell of Cs_2TeC_2. Bronze spheres denote Te, gray ones C, and dark-purple ones Cs. Notice the $[TeC_2]_\infty$ rods.

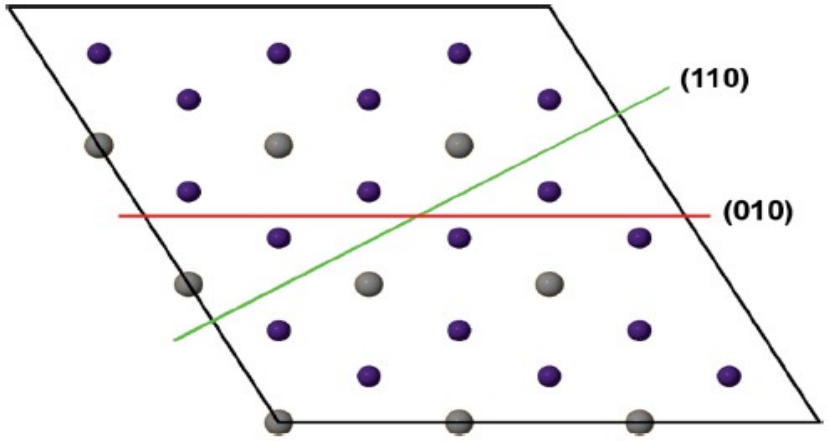


FIG. 2. (Color online) A top-down view of a 3 × 3 × 2 supercell of the hexagonal unit cell of Cs_2TeC_2. Color codes are identical with those in Fig. 1. The $[TeC_2]_\infty$ rodlike substructures are running perpendicularly to the plane viewed. The red line indicates the energetically preferred cleavage plane for the (010) surface running between two layers of Cs atoms, parallel with the rods, while the green line refers to the preferred cleavage plane for the (110) surface that involves $[TeC_2]_\infty$ rods directly exposed on the surface. Note that the (010) and (100) planes are identical.

Tuning the Workfunction of Cs_2Te by Acetylation

TABLE IV. Calculated (DFT) properties of photoemissive surfaces of acetylide compounds: Work functions (Φ), band gaps at the Γ-point $E_g(\Gamma)$, and surface energies (σ). Relaxed slabs refer to the relaxation of unrelaxed ones with the central two layers fixed. For h-Cs_2C_2(001) and Na_2TeC_2(010), $E_g(\Gamma) \approx 0.05$ eV has been found for a single band above E_F as well.

	Unrelaxed			Relaxed		
Compound and surface	Φ (eV)	$E_g(\Gamma)$ (eV)	σ (eV/Å^2)	Φ (eV)	$E_g(\Gamma)$ (eV)	σ (eV/Å^2)
o-Cs_2C_2(010)	2.80	1.25	0.023	–	–	–
h-Cs_2C_2(001)	2.56	1.14	0.027	–	–	–
Na_2PdC_2(001)	3.58	1.13	0.067	–	–	–
Na_2PdC_2(110)	3.73	1.65	0.029	4.17	2.34	0.024
Na_2PdC_2(010)	2.65	1.91	0.019	2.68	2.45	0.017
Cs_2PdC_2(001)	2.90	1.43	0.046	–	–	–
Cs_2PdC_2(110)	2.73	0.88	0.026	2.73	1.16	0.022
Cs_2PdC_2(010)	1.33	0.78	0.015	2.03	1.74	0.013
Na_2TeC_2(001)	3.40	1.03	0.029	–	–	–
Na_2TeC_2(110)	3.80	0.91	0.025	4.67	2.04	0.009
Na_2TeC_2(010)	2.75	1.43	0.015	2.68	1.34	0.015
Cs_2TeC_2(001)	3.71	1.86	0.022	–	–	–
Cs_2TeC_2(110)	2.77	0.77	0.020	2.98	1.38	0.019
Cs_2TeC_2(010)	1.71	1.00	0.013	2.44	1.63	0.009

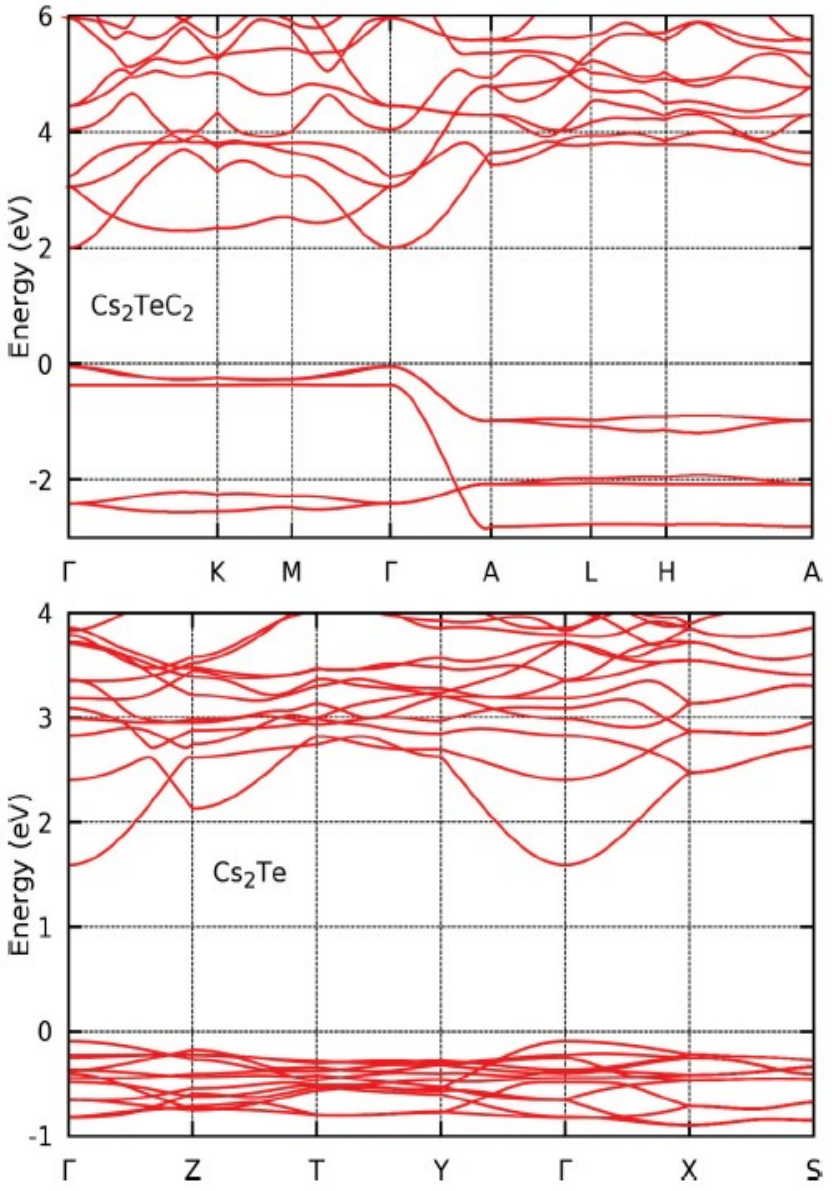
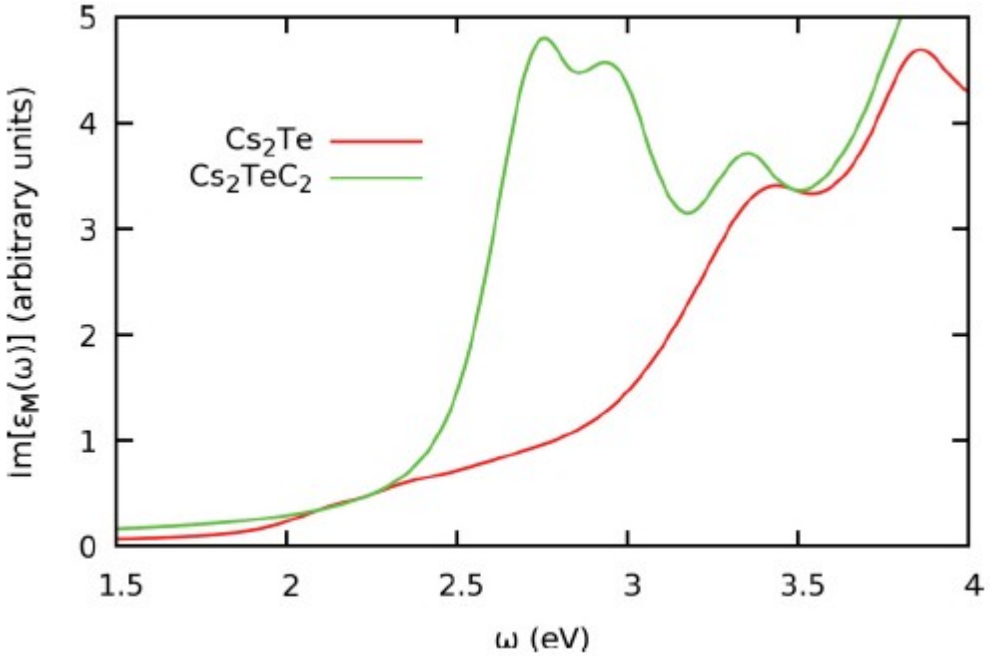
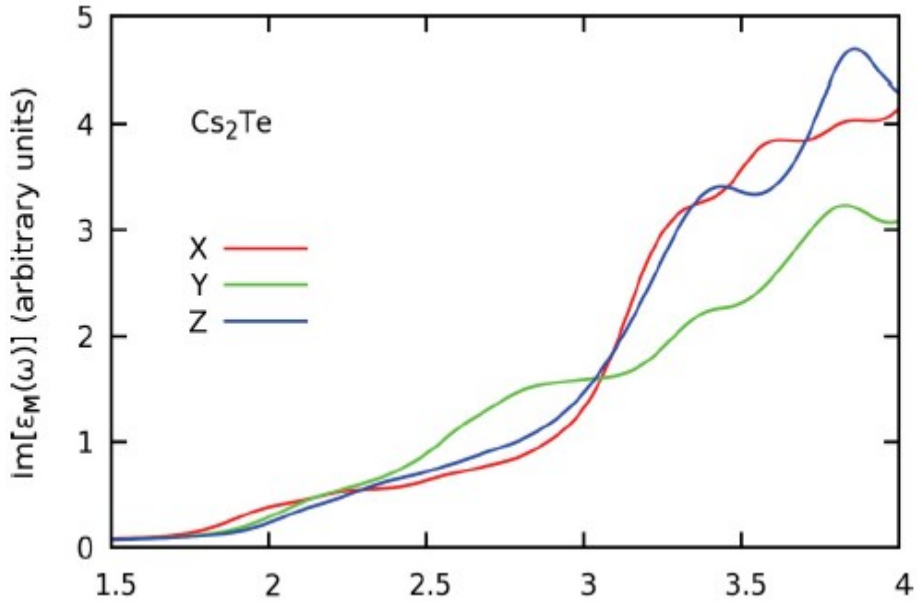
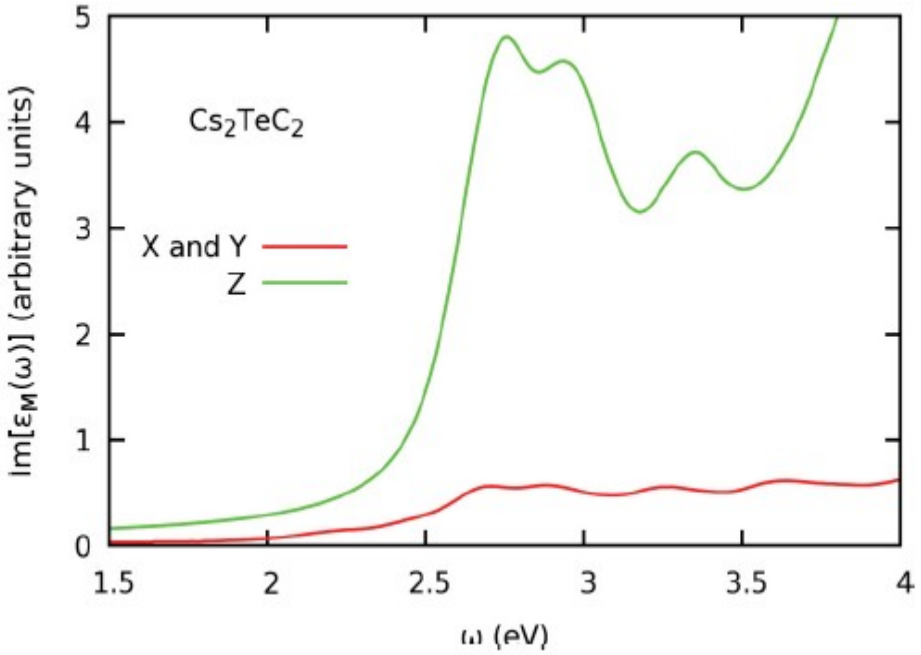


FIG. 4. (Color online) Band structures of Na_2TeC_2, Cs_2TeC_2, and Cs_2Te using the PBE[9] exchange-correlation functional. The k space was $14 \times 14 \times 14$ large. The Fermi energy is at 0 eV.

Calculated Optical Absorption Spectra of Cs_2Te and Cs_2TeC_2







Synthesis of A_2TeC_2

Direct reaction of Te powder and A_2C_2 (A=Li,Na,K,Rb,Cs) in a suitable reaction medium (typically completes in 15-30 minutes).

In collaboration with Prof. Aditya Unni, IIIT.

Searching for Low Workfunction and High QE Phases in the Cs-Te System: Cs_2Te_5

Motivation: Cs-Te alloy compounds may be easier to manufacture than Cs_2TeC_2 .
Cs_2Te_5 exists, easy to make and has 1D substructures similar to Cs_2TeC_2.

Reference: A. Ruth, K. Nemeth, K.C. Harkay et al., submitted to J. Appl. Phys.

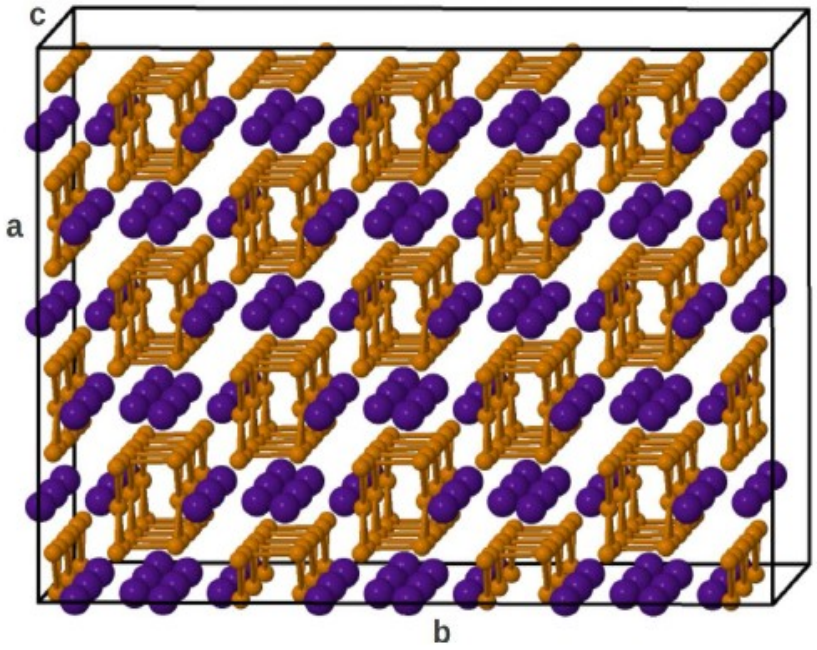


FIG. 1: A near top down view of a 3x3x3 supercell of the rectangular unit cell of Cs_2Te_5. Cell data are from Ref. 10. Bronze spheres denote Te, blue ones are Cs. Notice the quasi 1D $[Te_5^{2-}]_n$ polytelluride ions embedded in Cs matrix in the form of ≈ 4 Å wide wavy Te-ribbons, showed in detail in Fig. 2.

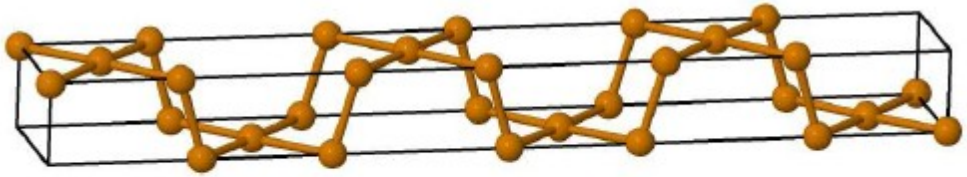
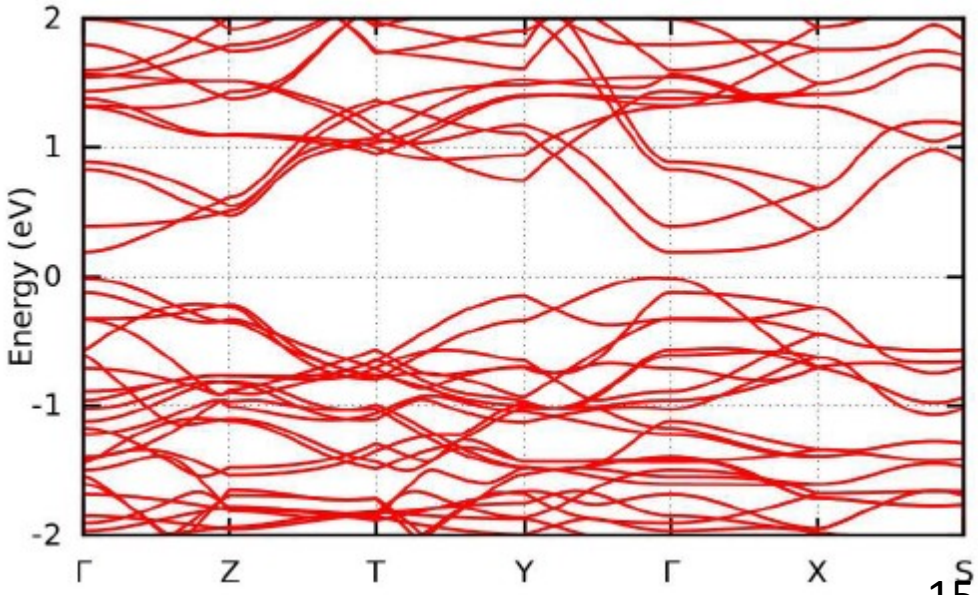


FIG. 2: An isolated Te-ribbon of the 3x3x3 supercell of Cs_2Te_5. In the wavy Te-ribbons, six-membered rings of Te in chair-conformation are connected via common vortices into quasi 1D chains.



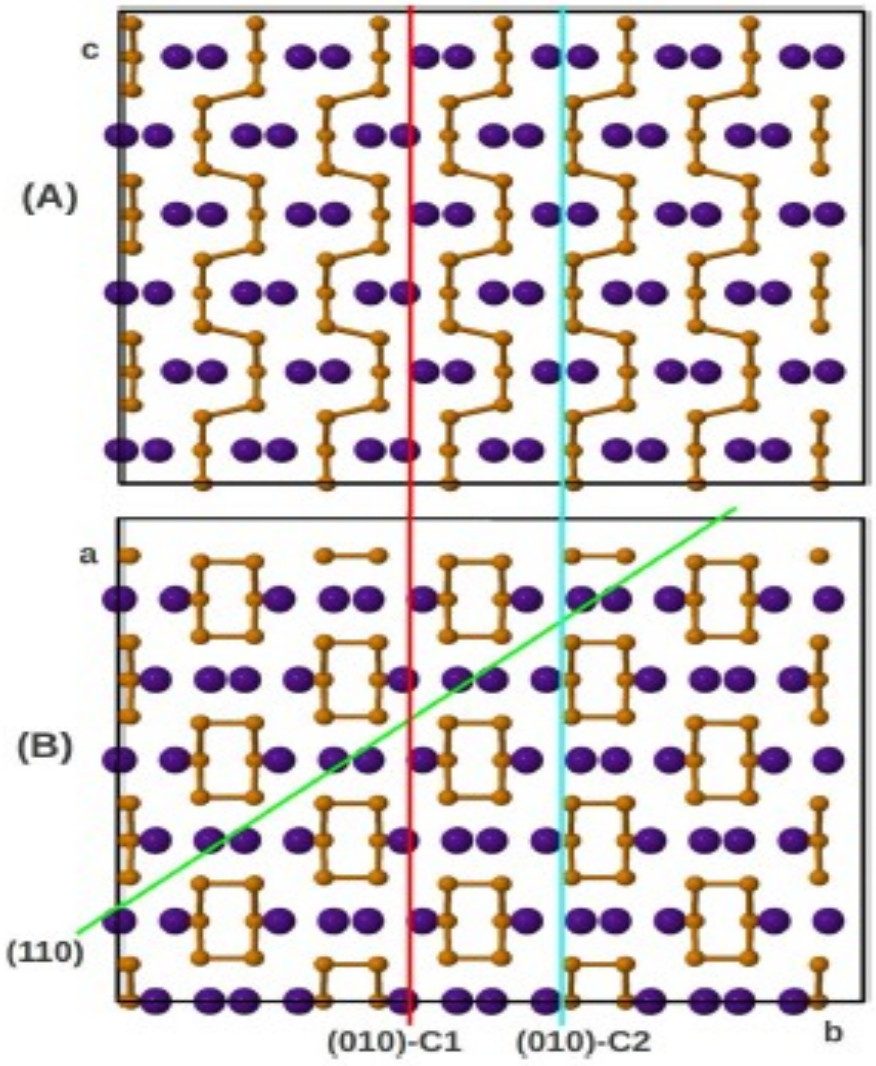
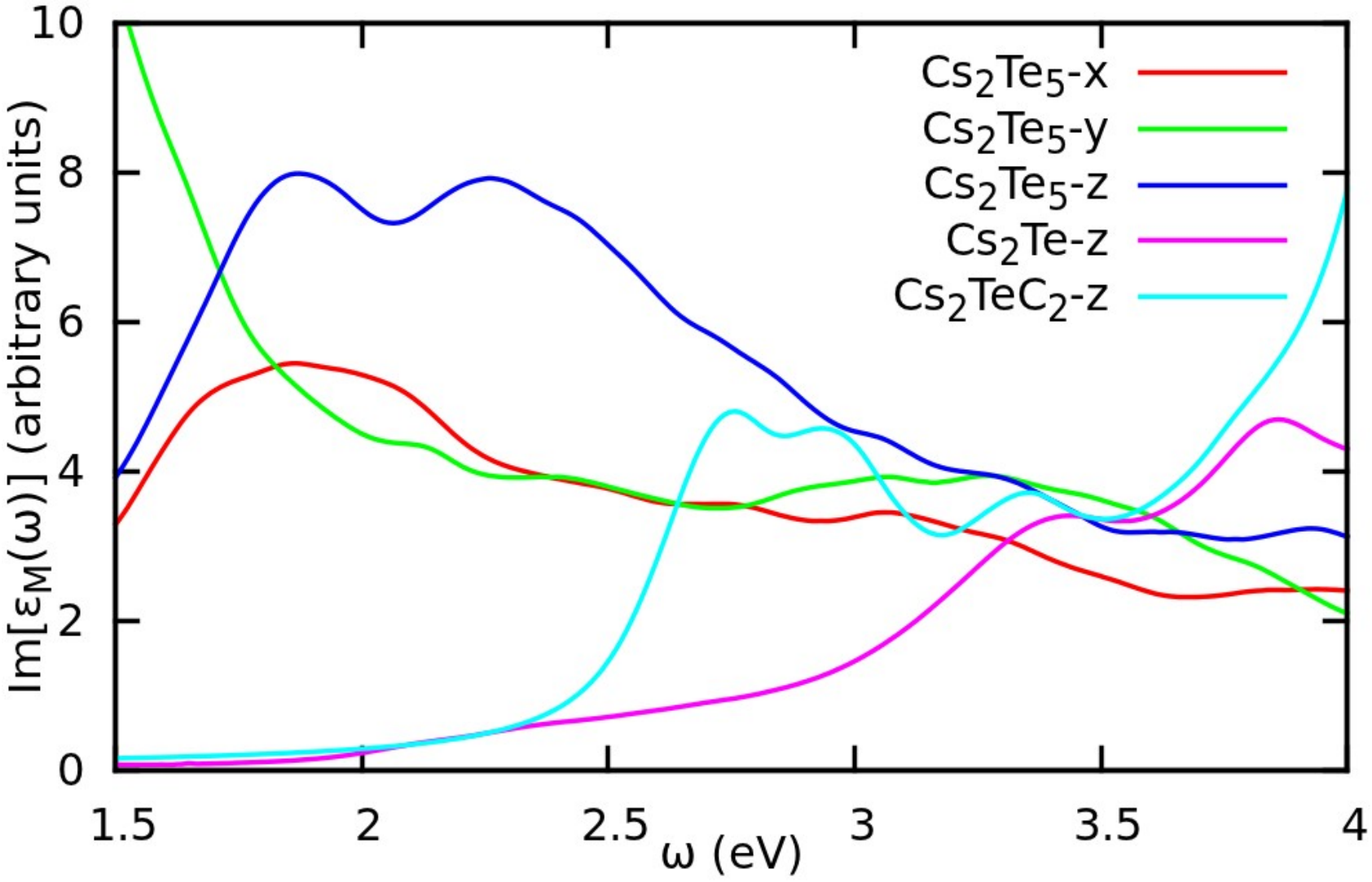


FIG. 5: Panels (A) and (B) show the (bc) and (ba) plane views of a 3x3x3 supercell of the Cs_2Te_5 crystal, respectively, where a, b and c denote the crystallographic axes. Only those crystal surfaces have been considered that do not cleave polytelluride ions and have small Miller indices. These are (110), (010)-C1 and (010)-C2. The (010)-C1 surface slab leaves some Te atoms directly exposed on both of its surfaces, while the (010)-C2 one has one fully Cs covered surface and one partially Cs covered one.

TABLE I: Calculated properties of Cs_2Te_5 surfaces: workfunctions (Φ), bandgaps at the Γ-point $E_g(\Gamma)$ and surface energies (σ). For the Cs_2Te_5(010)-C2 cleavage, data refer to the fully Cs-covered surface. The workfunction of this surface has been calculated both from the asymmetrically Cesiated Cs_2Te_5(010)-C2 slab ($\Phi = 1.87$ eV) and from the symmetrized (with additional Cs) and relaxed version of it ($\Phi = 1.97$ eV). The average surface energy of the asymmetrically Cesiated Cs_2Te_5(010)-C2 slab was 22.6 meV/Å^2, the contribution of the Cs-rich side is estimated to be close to the Cs_2Te_5(010)-C1 value ($\sigma = 7.1$ meV/Å^2).

surface	Φ (eV)	$E_g(\Gamma)$ (eV)	σ (meV/Å^2)
Cs_2Te_5(110)	3.22	0.3577	7.2
Cs_2Te_5(010)-C1	3.47	0.3344	7.1
Cs_2Te_5(010)-C2	1.87/1.97	0.0309	-
Cs_2Te_5(001)	4.70	0.0369	20.4

Calculated Optical Absorption Spectra of Cs_2Te, Cs_2TeC_2 and Cs_2Te_5



Summary and Conclusions

- Argonne-IIT-PNNL team taking a longer-term, first-principles approach to designing photocathodes with specific properties to meet requirements for future light sources.
- Focus has been on an ultrabright electron source: minimizing the intrinsic emittance, lowering the workfunction (more efficient use of drive laser), maintaining or improving QE. Higher robustness in an electron gun also a goal. Results have been published (PRL, PRB, JAP(submitted)), and inspired 2 patent applications.
- Synthesis and validation of predictions are underway for MgO:Ag and Cs_2TeC_2 systems. Synthesis of Cs_2Te_5 should be undertaken next.
- Challenges of scientific approach to photocathode development:
  - R&D should focus on well-defined requirements.
  - User facilities are focused on near-term development.
  - Multidisciplinary, team members have different goals.
  - Technology transfer.