Anomolous Workfunction Anisotropy in Ternary Acetylides: Applications to Photocathode R&D

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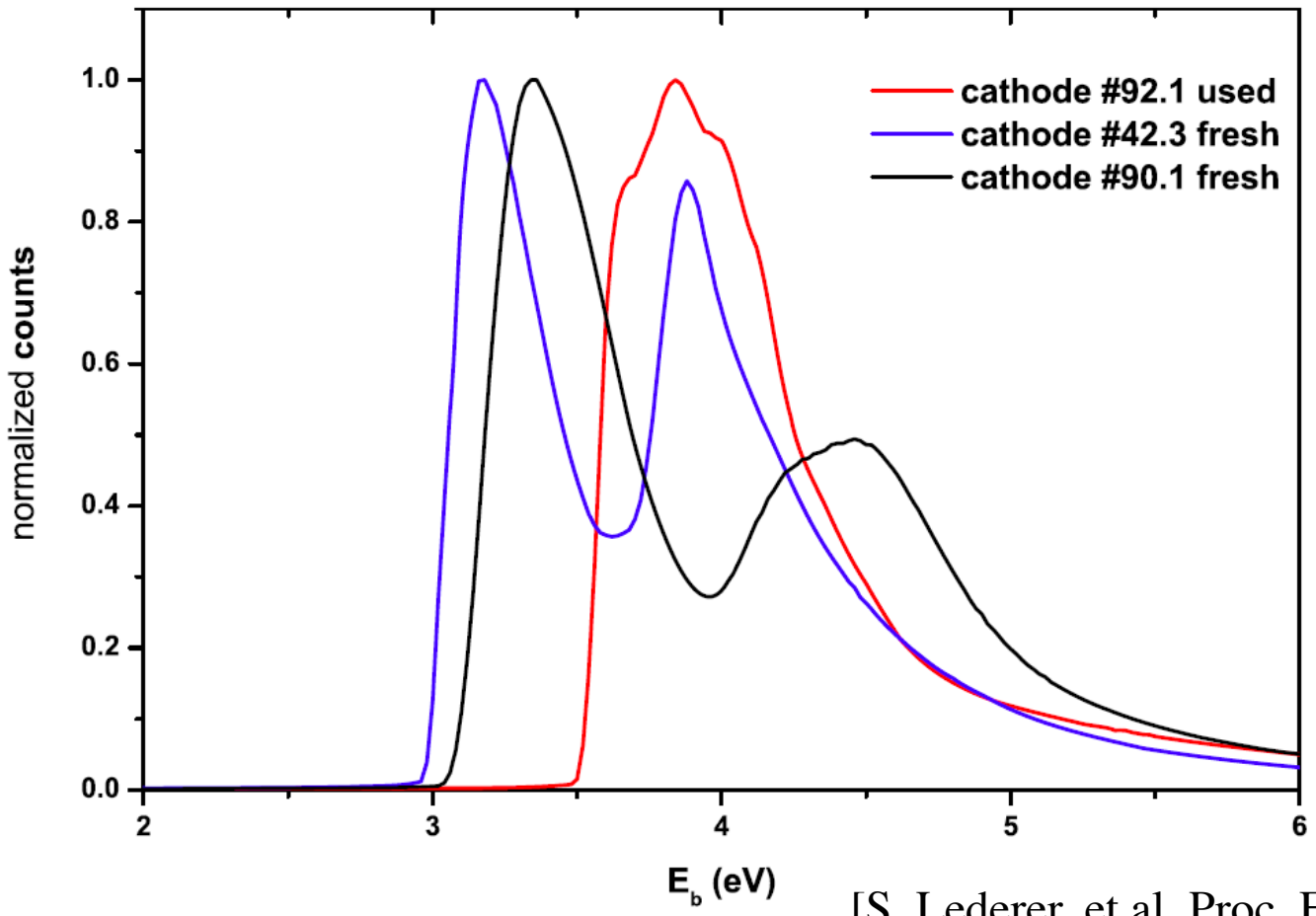
Outline

- Introduction: Aims of the research
- Ternary Acetylides: New class of photoemissive materials
- Unique 1D substructures
- Quantum Chemical DFT-based calculations
  - Workfunction, surface energies, optical absorption, and surface relaxation
- Advantages and Applications

Cesium Telluride (Cs_2Te) Photocathode



[S. Lederer, et.al, Proc. FEL 2007, p. 457]

- The workfunction of Cesium Telluride photocathodes increases as the cathode is used by up to 1 eV.
- Only partial rejuvenation is possible.

Effect of small gases on Cs_2Te Quantum Efficiency

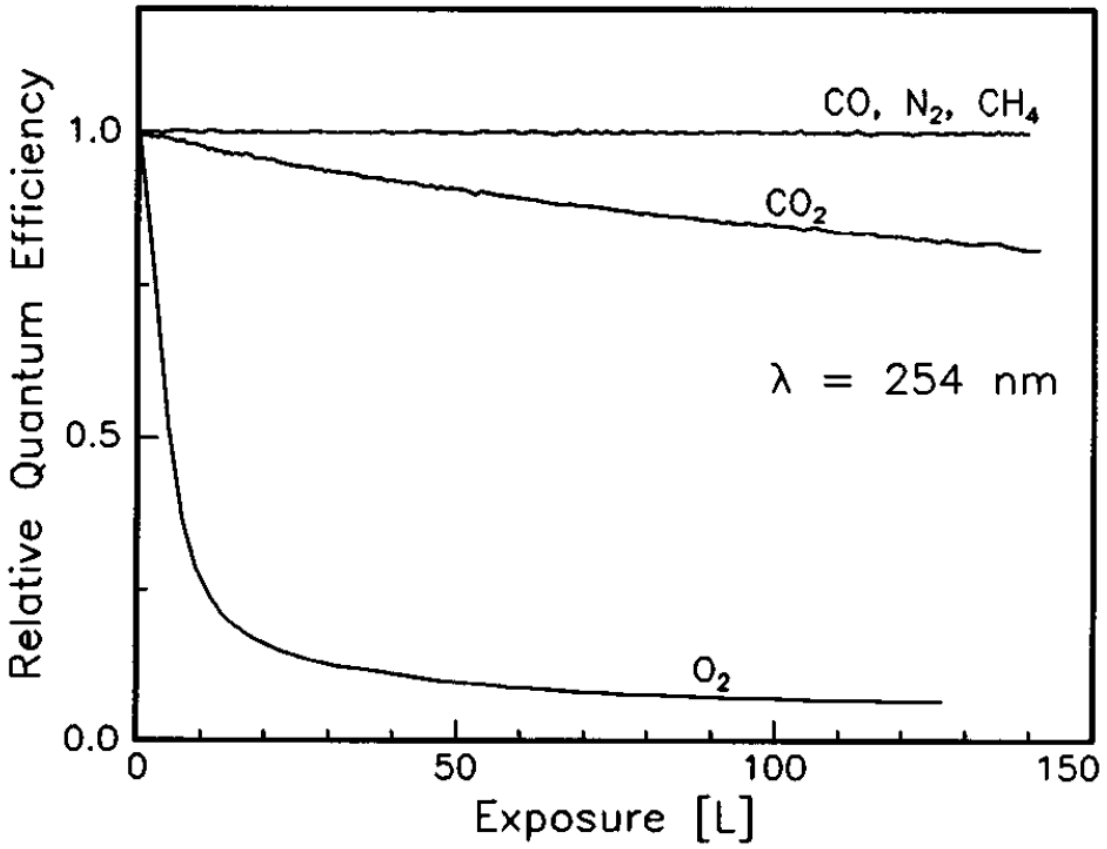


FIG. 7. Quantum efficiency drop for the 254 nm radiation of the photocathode exposed to different gases.

[A. di Bona, et.al. J.Appl.Phys. 80 (5), 1996]

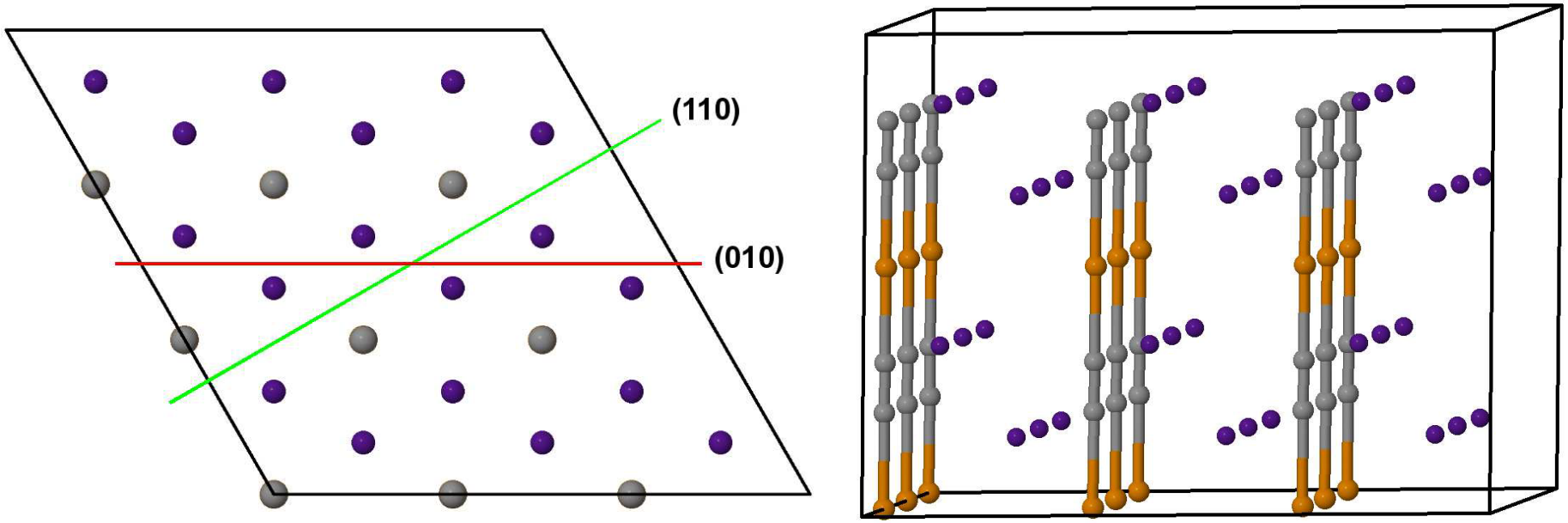
CO, N_2, CH_4, 0_2, and CO_2 were investigated in order to simulate practical vacuum condititions .

- However, acetylene gas was not investigated.
- Acetylene is fairly reactive, easily losing its hydrogens, which takes electrons away from the material in contact. This forms "acetylides," containing the acetylide anion [:C:::C:]2-, commonly denoted as C_2^{2-}

Proposed synthesis routes

$$Cs_2Te(cr) + C_2H_2(g) \rightarrow Cs_2TeC_2(cr) + H_2(g) \ , \Delta E = +1.1 \text{ eV}$$

$$Cs_2C_2(cr) + Te(cr) \rightarrow Cs_2TeC_2(cr) \ , \Delta E = -0.95 \text{ eV}$$



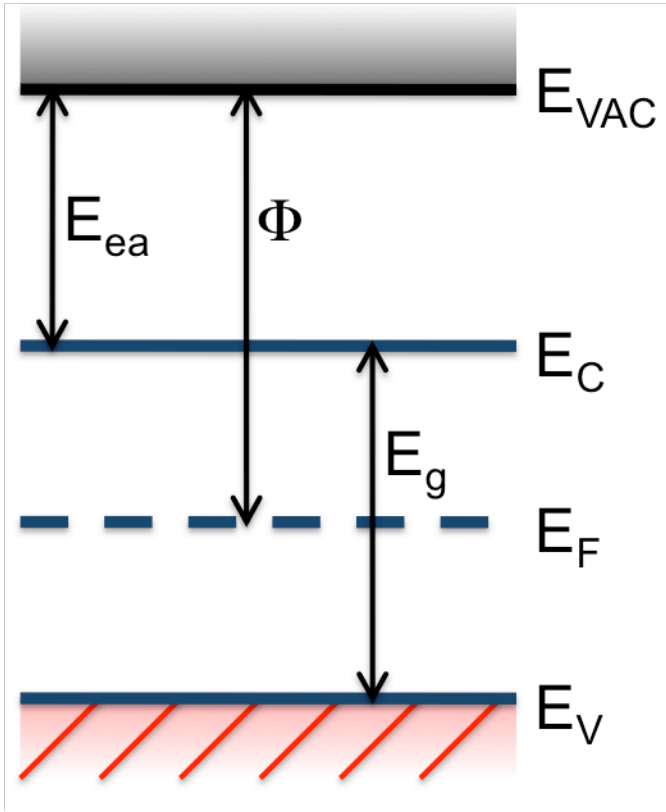
Top (left) and side (right) view of Cs_2TeC_2. Note the hexagonal packing of $[TeC_2]_\infty$ rods. Dark purple indicates Cs, grey indicates C, and bronze indicated Te.

Calculating Workfunctions

- Workfunction is the energy required to move an electron from the bulk crystal into the vacuum:

$$\Phi = \Delta V_{el} - E_f$$

where ΔV_{el} is the rise in electrostatic potential as the electron moves through the surface of the crystal, and E_f (Fermi Energy) is the highest available electron energy.



In the simulations we must avoid finite size effects which can systematically distort our results. This is effectively done through averaging surface electrostatic potentials, and referencing all surface values to bulk values where finite size effects are avoided. (C.J. Fall *et al,* J. Phys: Condensed Matter. 1999)

Validation of DFT, PBE functional

TABLE I: Validation of the a, b and c lattice parameters on several test systems using the PBE density functional, as described in the discussion. Orthorhombic and hexagonal Cs_2C_2 are denoted as o-Cs_2C_2 and h-Cs_2C_2, respectively, with structural parameters not very accurately determined due to the coexistence of the two phases at any temperature.

Compound, space-group & reference	Lattice Parameters (Å) EXPT a	EXPT b	EXPT c	DFT a	DFT b	DFT c
Cs ($Im\bar{3}m$)[13]	6.067	6.067	6.067	6.067	6.067	6.067
Te ($P3_121$) [14]	4.526	4.526	5.920	4.458	4.458	5.925
Cs_2Te (Pnma)[15]	9.512	5.838	11.748	9.109	5.871	11.494
C ($Fd\bar{3}m$)[16]	3.567	3.567	3.567	3.573	3.573	3.573
Na_2C_2 ($I4_1/acd$)[17]	6.778	6.778	12.740	6.941	6.941	13.027
o-Cs_2C_2 (Pnma)[18]	9.545	5.001	10.374	9.826	5.061	10.491
h-Cs_2C_2 ($P\bar{6}2m$)[18]	8.637	8.637	5.574	8.728	8.728	6.048
$CsAgC_2$($P4_2mmc$)[6]	5.247	5.247	8.528	5.317	5.317	9.036
Na_2PdC_2 ($P\bar{3}m1$)[5]	4.464	4.464	5.266	4.632	4.632	5.284
Cs_2PdC_2 ($P\bar{3}m1$)[4]	5.624	5.624	5.298	5.804	5.804	5.265
Na_2TeC_2 ($P\bar{3}m1$)	-	-	-	4.767	4.767	6.102
Cs_2TeC_2 ($P\bar{3}m1$)	-	-	-	5.820	5.820	6.152

TABLE II: Validation of C-C and M-C distances (M is transition-metal or metalloid element).

Compound, Space-group & ref.	d(C-C) (Å) EXPT	d(C-C) (Å) DFT	d(M-C) (Å) EXPT	d(M-C) (Å) DFT
C ($Fd\bar{3}m$)[16]	1.544	1.547	-	-
C_2H_2 (gas) [19]	1.203	1.203	-	-
Na_2C_2 (I41/acd) [17]	1.204	1.261	-	-
o-Cs_2C_2 (Pnma) [18]	1.385	1.269	-	-
h-Cs_2C_2 ($P\bar{6}2m$)[18]	0.934	1.267	-	-
$CsAgC_2$ ($P4_2mmc$) [6]	1.216	1.249	2.016	2.034
Na_2PdC_2 ($P\bar{3}m1$) [5]	1.262	1.271	2.019	2.006
Cs_2PdC_2 ($P\bar{3}m1$) [4]	1.260	1.280	2.019	1.993
Na_2TeC_2 ($P\bar{3}m1$)	-	1.259	-	2.422
Cs_2TeC_2 ($P\bar{3}m1$)	-	1.257	-	2.452

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

Compound and surface	Φ (eV) EXPT	Φ (eV) DFT	$E_g(\Gamma)$ (eV) DFT	σ (eV/Å^2) DFT
Cs(100)	2.14 [20]	2.00	0.29	0.005
Te(001)	4.95 [20]	5.02	0.54	0.036
Cs_2Te(001)	2.90-3.0 [21]	3.08	0.77	0.015
Cs_2Te(010)	2.90-3.0 [21]	2.90	1.04	0.014
(Cs)Na_3KSb	1.55 [22]	-	-	-
K_2CsSb	1.9-2.1 [23, 24]	-	-	-

Calculated surface properties (DFT), No surface relaxation

Compound and surface	unrelaxed 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
Na_2PdC_2(010)	2.65	1.91	0.019
Cs_2PdC_2(001)	2.90	1.43	0.046
Cs_2PdC_2(110)	2.73	0.88	0.026
Cs_2PdC_2(010)	1.33	0.78	0.015
Na_2TeC_2(001)	3.40	1.03	0.029
Na_2TeC_2(110)	3.80	0.91	0.025
Na_2TeC_2(010)	2.75	1.43	0.015
Cs_2TeC_2(001)	3.71	1.86	0.022
Cs_2TeC_2(110)	2.77	0.77	0.020
Cs_2TeC_2(010)	1.71	1.00	0.013

General Trends

- (010) surface are the most stable and show the lowest workfunctions
- Approximately 1-2 eV reduction in workfunction between (001) and (010) surfaces.
- Changing alkali atom has effect on workfunction and bandgaps

Differences in Metalloid and Transition Metal Bond Strength

Metalloid (Te)

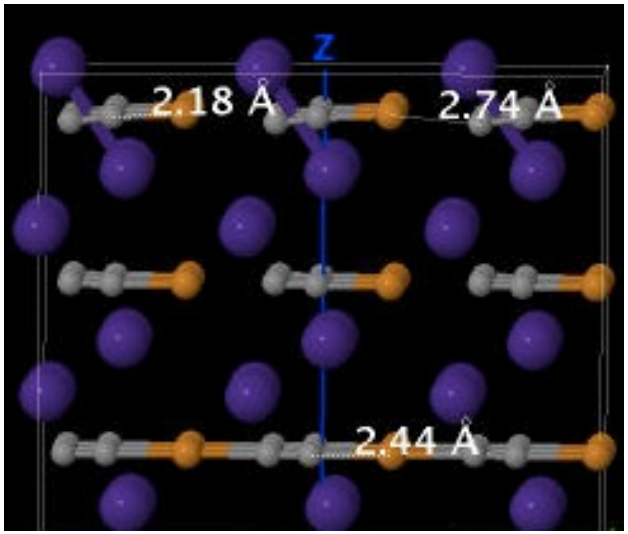
Compound and surface	unrelaxed Φ (eV)	unrelaxed $E_g(\Gamma)$ (eV)	unrelaxed σ (eV/Å^2)
$Cs_2TeC_2(001)$	3.71	1.86	0.022
$Cs_2TeC_2(110)$	2.77	0.77	0.020
$Cs_2TeC_2(010)$	1.71	1.00	0.013

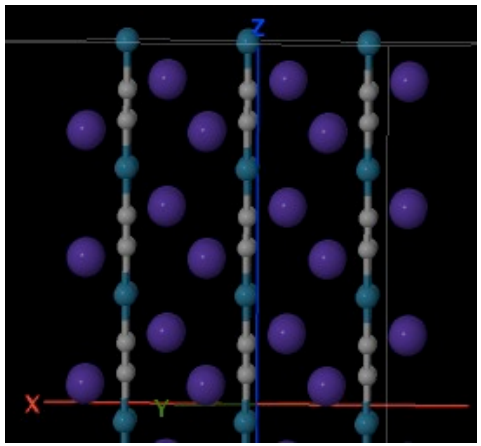
Transition Metal (Pd)

Compound and surface	unrelaxed Φ (eV)	unrelaxed $E_g(\Gamma)$ (eV)	unrelaxed σ (eV/Å^2)
$Cs_2PdC_2(001)$	2.90	1.43	0.046
$Cs_2PdC_2(110)$	2.73	0.88	0.026
$Cs_2PdC_2(010)$	1.33	0.78	0.015

Effect of Surface Relaxation on C-M bond lengths

$Cs_2TeC_2(010)$

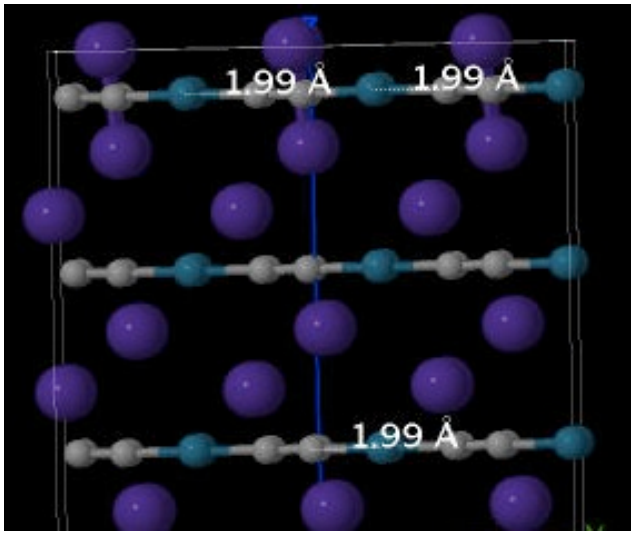




Rods Surface Perpendicular

$Cs_2PdC_2(001)$

$Cs_2PdC_2(010)$

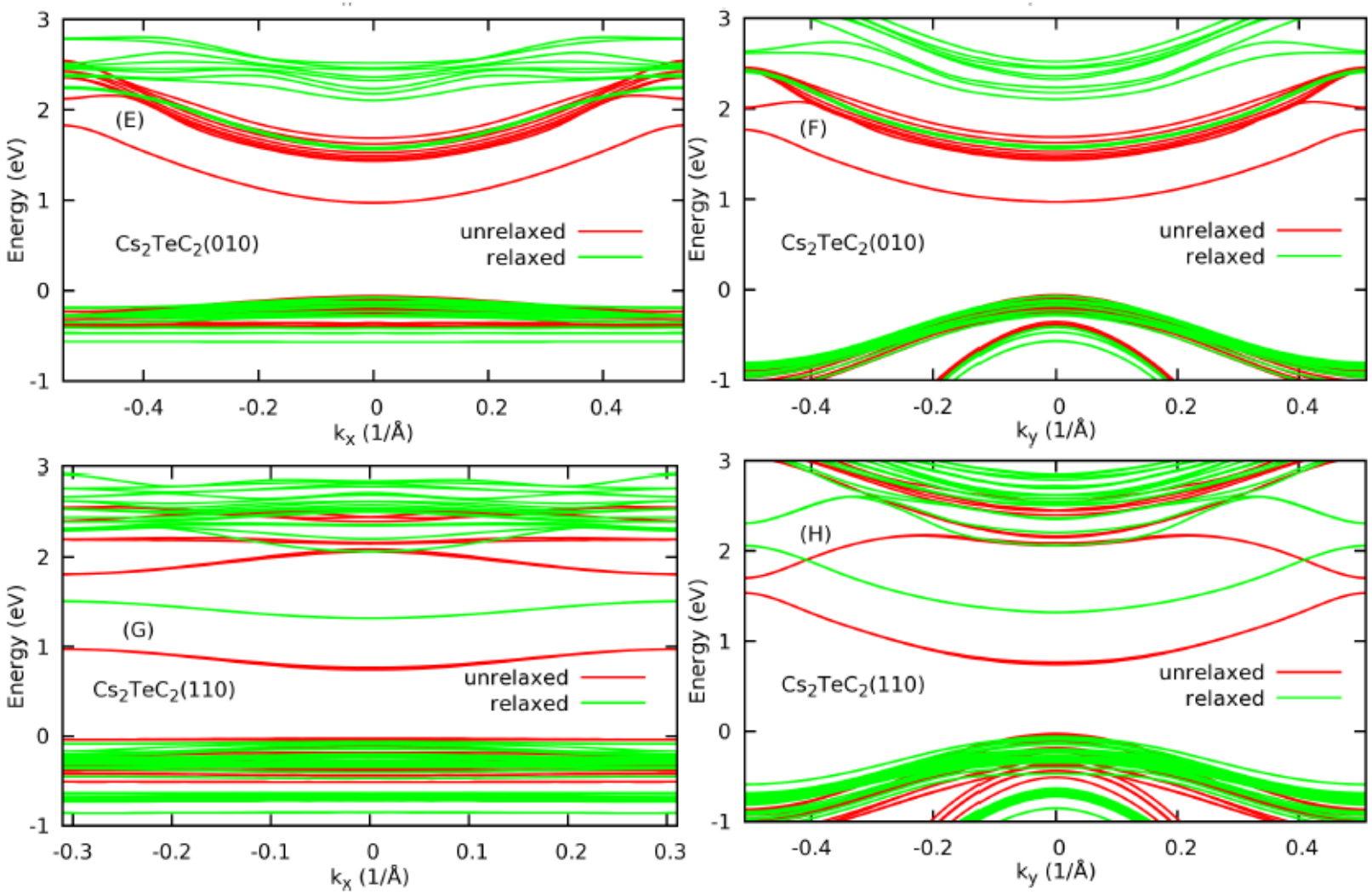


Effect of Surface Relaxation

Compound and surface	unrelaxed Φ (eV)	unrelaxed $E_g(\Gamma)$ (eV)	unrelaxed σ (eV/Å^2)	relaxed Φ (eV)	relaxed $E_g(\Gamma)$ (eV)	relaxed 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

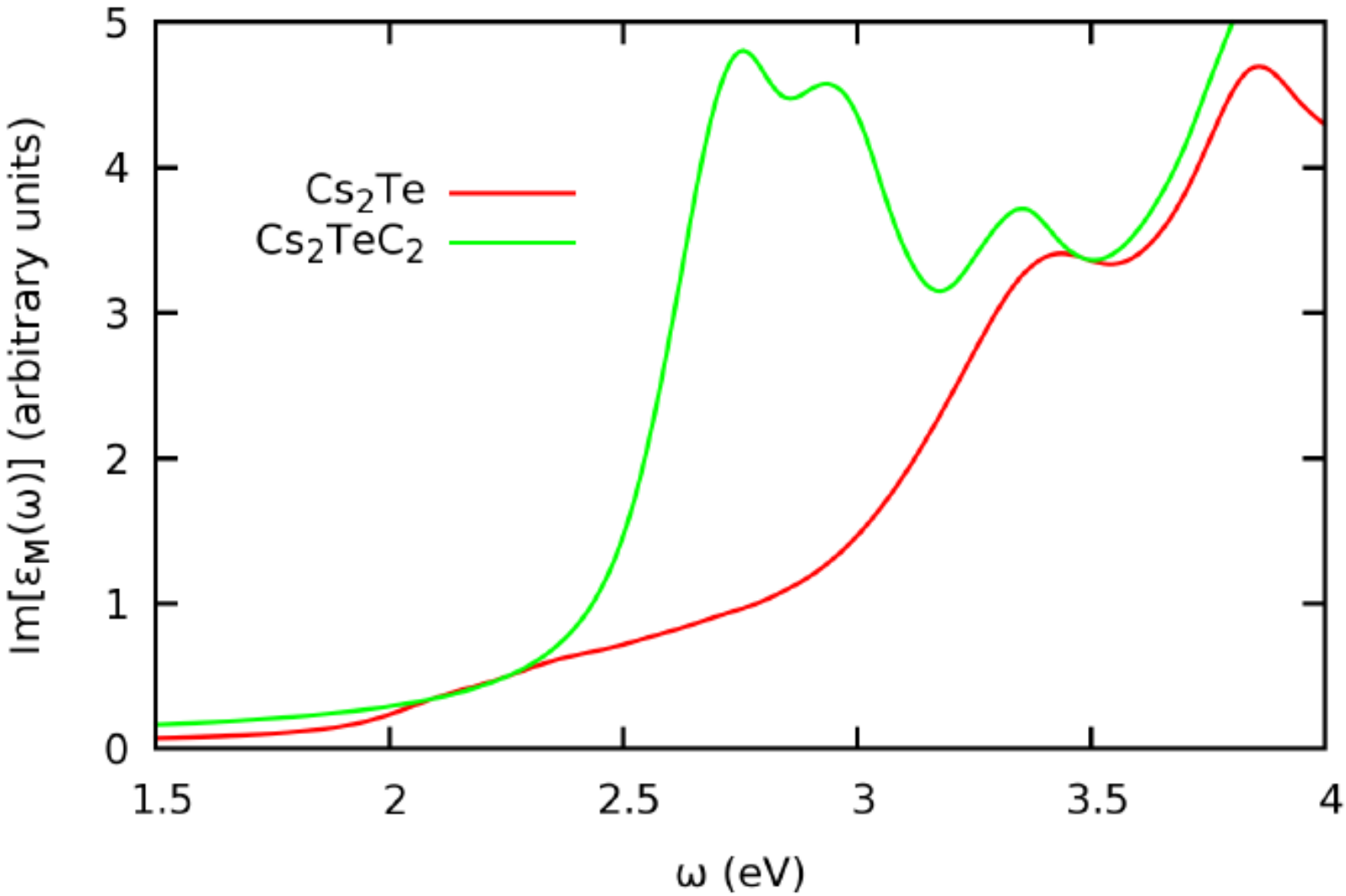
- Surface relaxations increase the work-function but maintain a >1eV reduction compared to expt and simulated workfunctions of cesium telluride
- The per atom change in energy for surface relaxation is comparable to thermal energy indicating both relaxed and unrelaxed geometries contribute to observed workfunctions.

Effect of surface relaxation on band structure



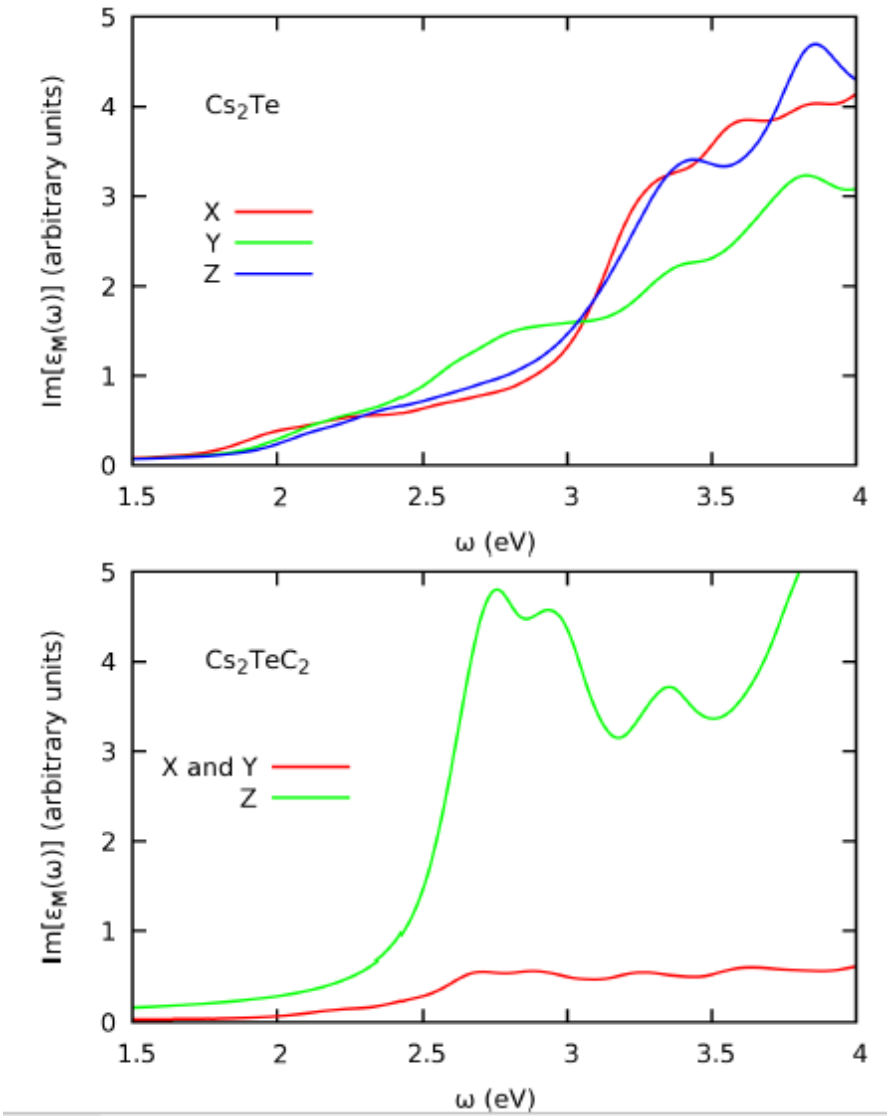
Electronic bands of surfaces with surface parrallel rods (010) and (110). Rods are in the y-direction. The occupied bands (E<0) are not affected by surface relaxations, however surface relaxation has pronounced effects on unoccupied bands .

Comparison of optical absorption spectra



Optical absorption spectra of bulk cesium telluride and cesium telluride carbide. Polarization of light is along the main crystallographic axis (c-axis of ceisum telluride and parrallel to the rods for cesium telluride carbide.

Anisotropy in Optical Absorption



Polarization dependent optical absorption spectra. We observe an order of magnitude increase in optical absorption for cesium telluride carbide when the polarization of light is orthogonal (bottom, red) and parrallel (bottom, green) to the rods. No comparably large anisotropy is observed in cesium telluride.

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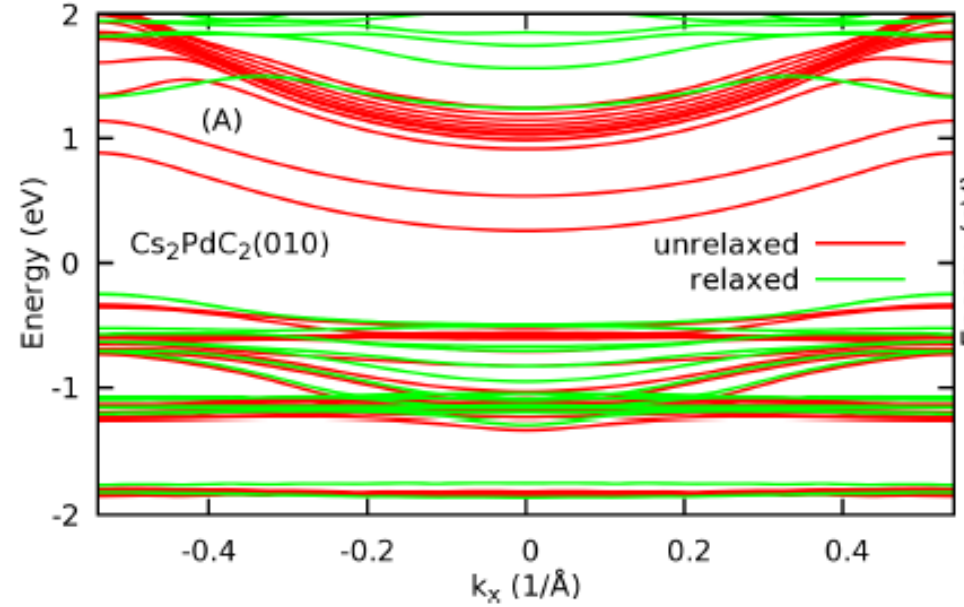
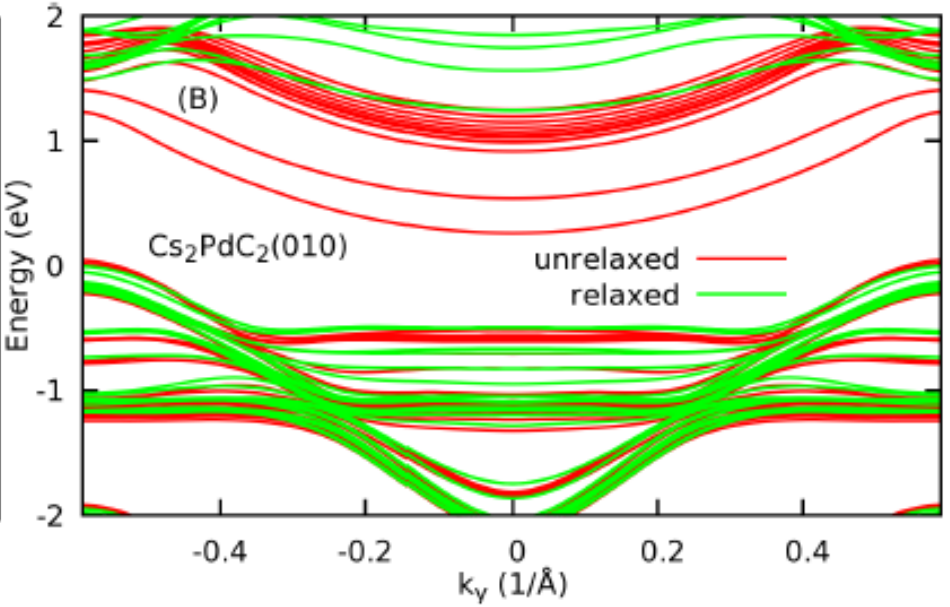
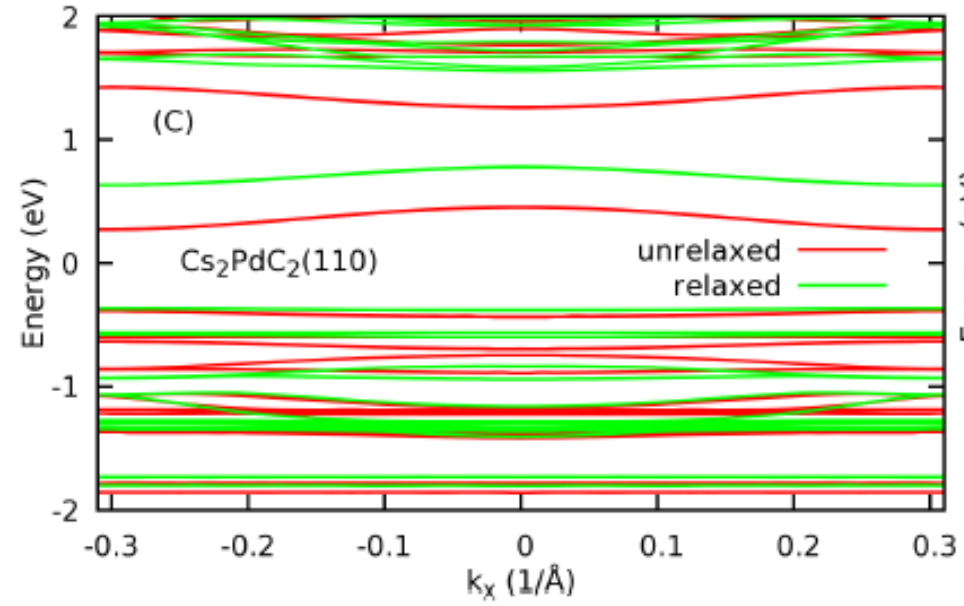
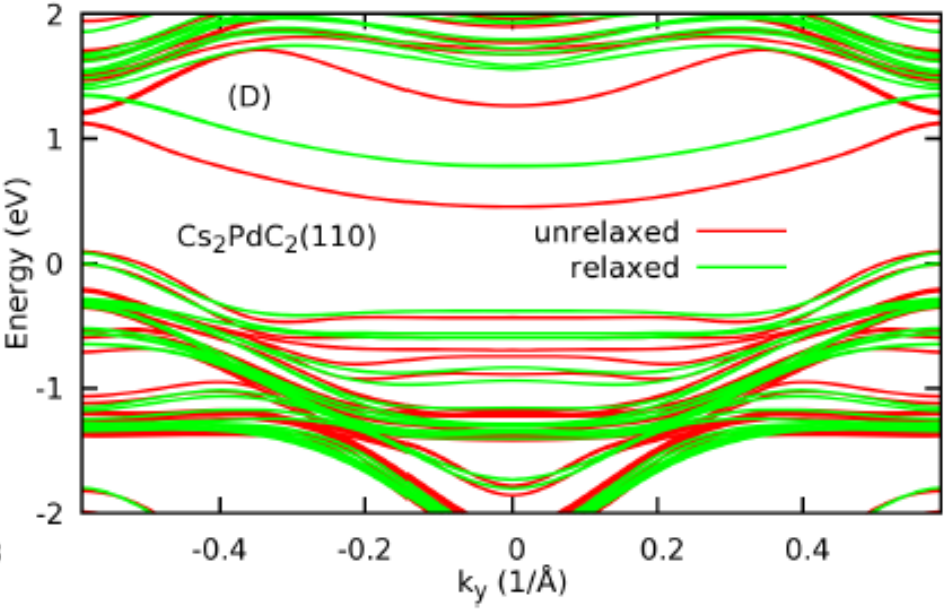
- Richard Rosenberg (ANL)
- George Srajer (ANL)


(A)
Cs2PdC2(010)
unrelaxed
relaxed
Energy (eV)
kx (1/Å)


(B)
Cs2PdC2(010)
unrelaxed
relaxed
Energy (eV)
ky (1/Å)


(C)
Cs2PdC2(110)
unrelaxed
relaxed
Energy (eV)
kx (1/Å)


(D)
Cs2PdC2(110)
unrelaxed
relaxed
Energy (eV)
ky (1/Å)

Density of States: Comparison of Cs_2Te and Cs_2TeC_2