

Redesigning Cs_2Te : Work Function Lowering and Quantum Efficiency Preservation via Acetylation

J. Zsolt Terdik, Károly Németh, Katherine Harkay
Argonne

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Outline

- Introduction
- Ternary acetylides: a new class of photoemissive materials
- Numerical calculations of electronic properties using DFT
- Synthesis status
- Summary



Introduction (1)

- Ultra-bright photocathodes are a key technology for the development of future light sources.
- It would be very interesting if one could design or tune specific photocathode properties for a given application, for example:
 - Work function: relaxes laser requirements if QE preserved
 - QE: improves brightness if work function preserved
 - Intrinsic emittance: improves brightness if QE is preserved
 - Reliability, robustness (vacuum, E-field, field emission): improves operation cost/complexity

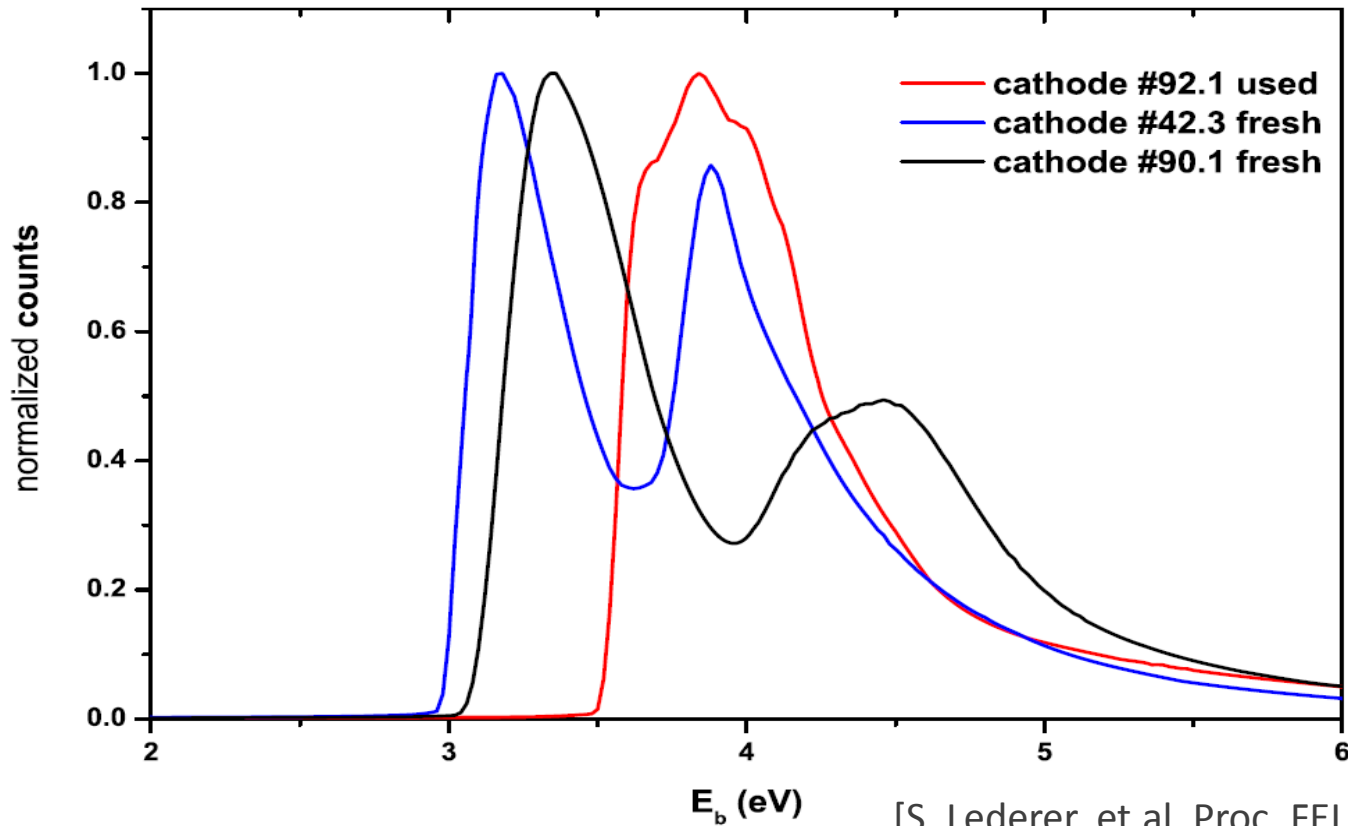


Introduction (2)

- Argonne has expertise in fabricating high-QE cesium telluride (Cs_2Te) cathodes, routinely achieving $> 10\%$ initial QE, and Cs_2Te is relatively robust.
- Thinking of ways to modify the workfunction of Cs_2Te while preserving its QE led to the investigation of a class of materials known as ternary acetylides.
- Electronic properties of candidate systems have been computed using quantum-chemical Density Functional Theory (DFT)-based surface-physics calculations (PWSCF, YAMBO).
- Next step is ongoing:
 - Synthesis: develop & test hypotheses for chemical reactions
 - Characterization: verify that the desired compound was synthesized and that it performs as predicted



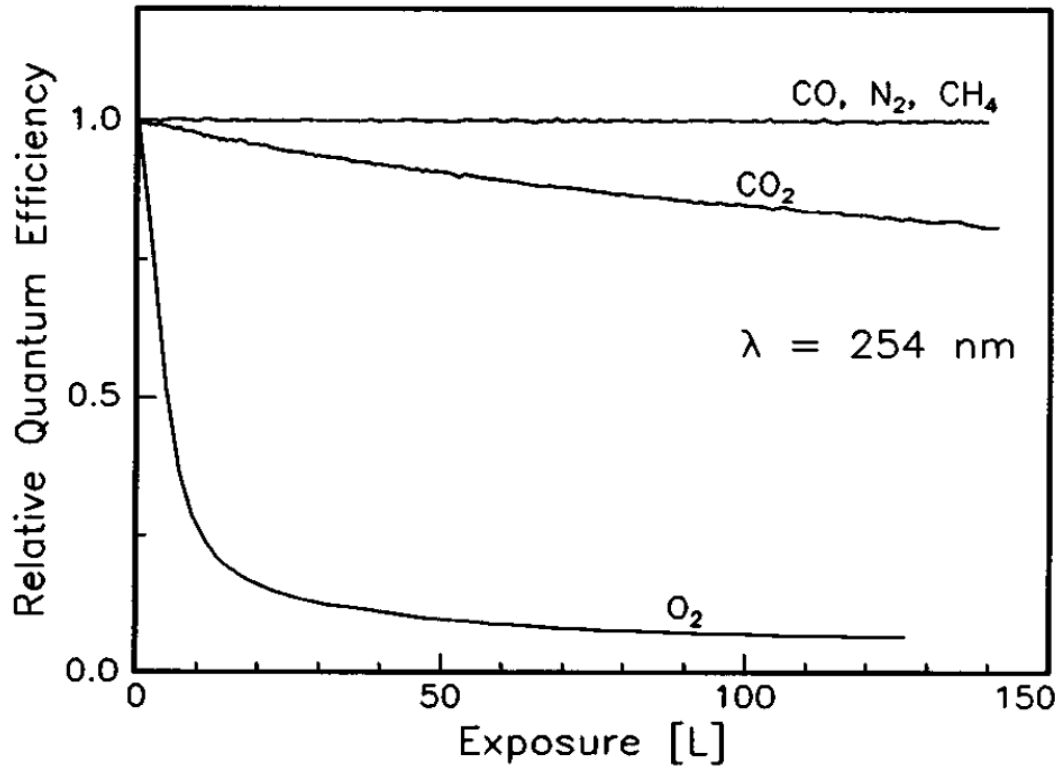
Photoemission from Cs₂Te cathode



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

- Workfunction increases, by up to 1 eV, and QE decreases as Cs₂Te ages. Typically only partial rejuvenation is achieved.
- Pushing the Cs₂Te photoemission (workfunction) to visible/infrared would have tremendous advantages.

Effect of small gas molecules on Cs₂Te quantum efficiency



- O₂, CO₂, CO, N₂ and CH₄ were investigated in order to simulate practical vacuum conditions.
- However, acetylene gas, C₂H₂ was not investigated.
- **What about reacting Cs₂Te with acetylene?**
- Acetylene is fairly reactive, easily losing its hydrogens, which captures electrons from the material in contact. This forms “acetylides,” containing the acetylide anion [C₂]²⁻, commonly denoted as C₂²⁻.

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]

A₂MC₂ Type Ternary Acetylides

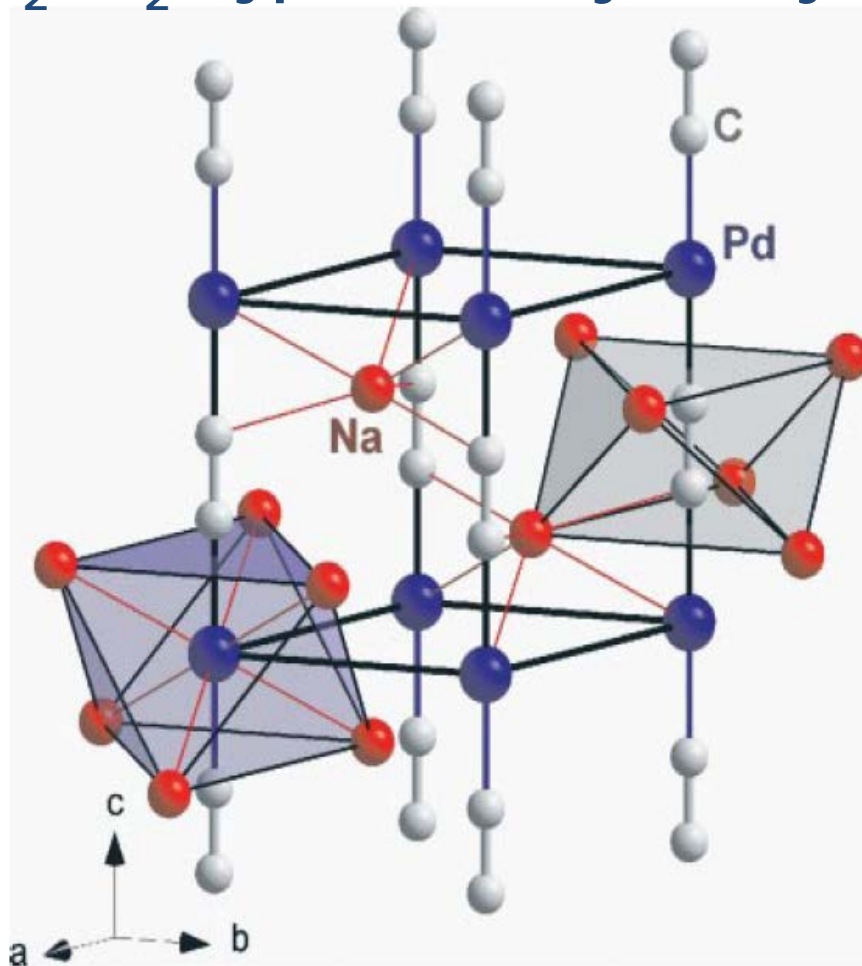


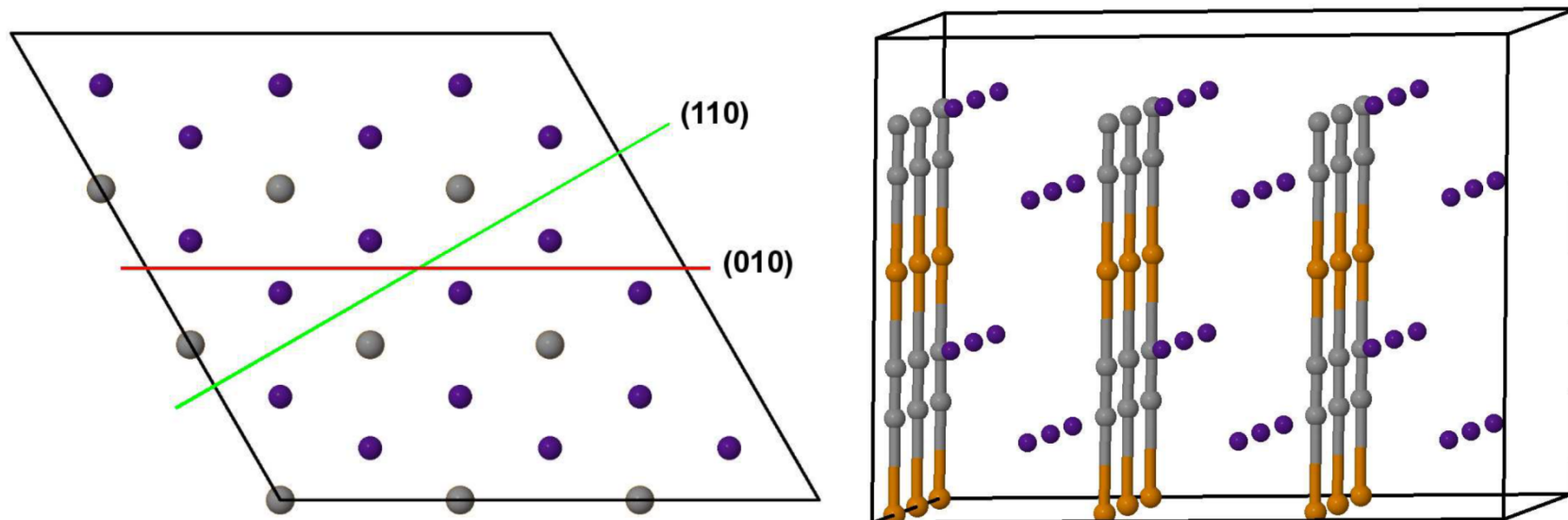
Fig. 3 Crystal structure of Na₂PdC₂ (P $\bar{3}$ m1, Z = 1). Selected interatomic distances are: Pd–C 200.2(2) pm, Na–Pd 296.8(2) pm, Na–C 263.1(1) pm, C–C 126.3(3) pm.

[Fig: U. Ruschewitz, Z. Anorg. Allg. Chem. 632, 705, 2006.]

- Unique 1D substructures, where A=alkali metal and M=transition metal or metalloid, C=carbon.
- All known A₂MC₂ are colored semiconductors with 2.1-2.8 eV direct band gaps.
- Synthesized so far: M ∈ [Pt, Pd] and A ∈ [Na, K, Rb, Cs].
- **We investigated acetylated Cs₂Te, where M=Te and A=Cs**
- Completely new class of materials for photophysics and low-work-function applications (e.g., field-emission displays).

Provisional patent application filed: K. Nemeth et al.

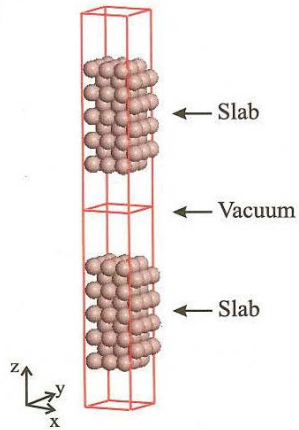
Proposed synthesis routes



Top (left) and side (right) view of Cs₂TeC₂. Note the hexagonal packing of [TeC₂]_∞ rods. Dark purple indicates Cs, grey indicates C, and bronze indicated Te.

Validation of DFT (1): properties

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Phys. Rev. B 86, 035142 (2012).



- Good agreement for surface properties of Cs, Te, Cs₂Te.

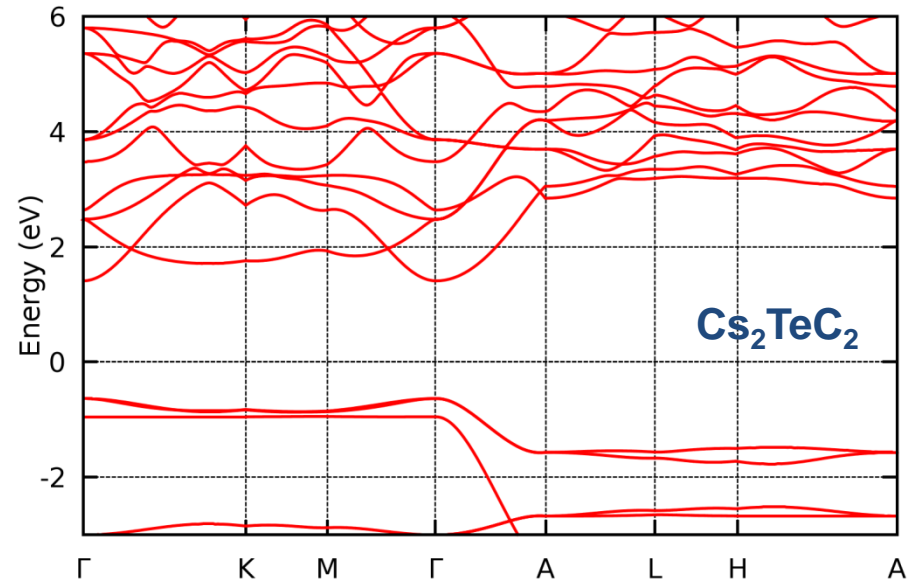
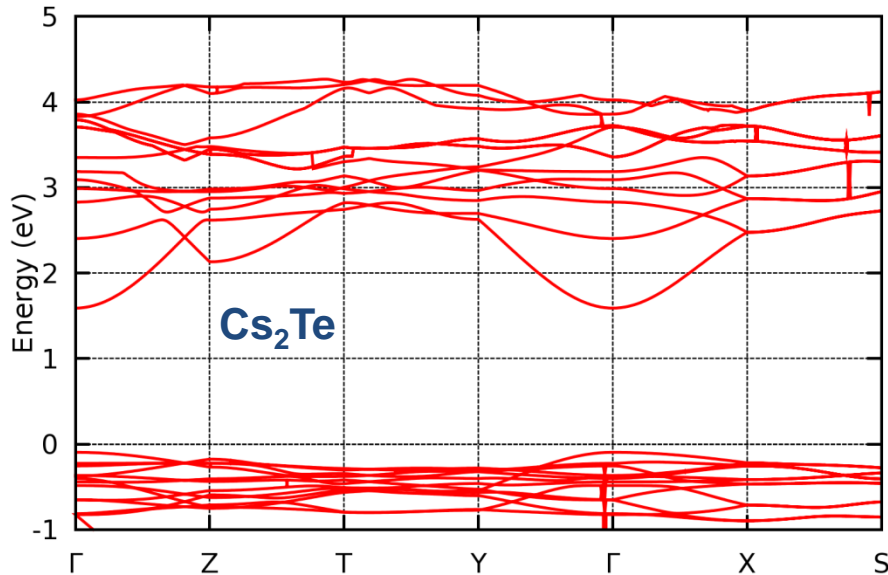
TABLE III: Experimental and calculated (DFT) properties of photoemissive surfaces of validation materials: workfunctions (Φ), bandgaps at the Γ -point $E_g(\Gamma)$ and surface energies (σ).

Compound and surface	Φ (eV)		$E_g(\Gamma)$ (eV)	σ (eV/Å ²)
	EXPT	DFT		
Cs(100)	2.14 [21]	2.00	0.29	0.005
Te(001)	4.95 [21]	5.02	0.54	0.036
Cs ₂ Te(001)	2.90-3.0 [22]	3.08	0.77	0.015
Cs ₂ Te(010)	2.90-3.0 [22]	2.90	1.04	0.014
(Cs)Na ₃ KSb	1.55 [23]	-	-	-
K ₂ CsSb	1.9-2.1 [24, 25]	-	-	-

Fig. courtesy A. Michaelides, M. Scheffler

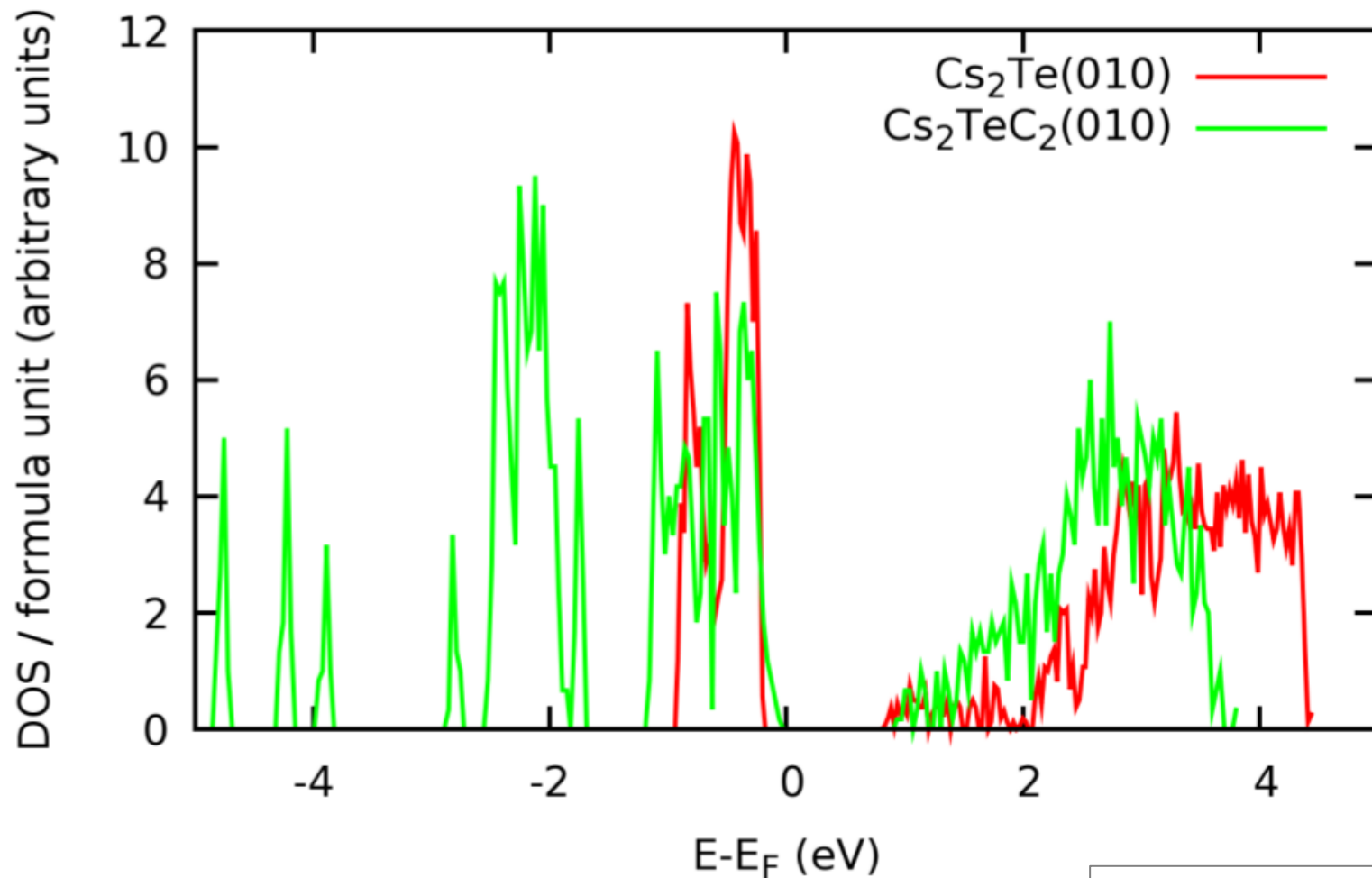
- Also computed were the a,b,c lattice parameters and C-C and M-C distances for several test systems, which compared well with experiment.
- In the simulations, finite size effects, which can systematically distort the results, were avoided through averaging surface electrostatic potentials, and referencing 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 (2): band structure



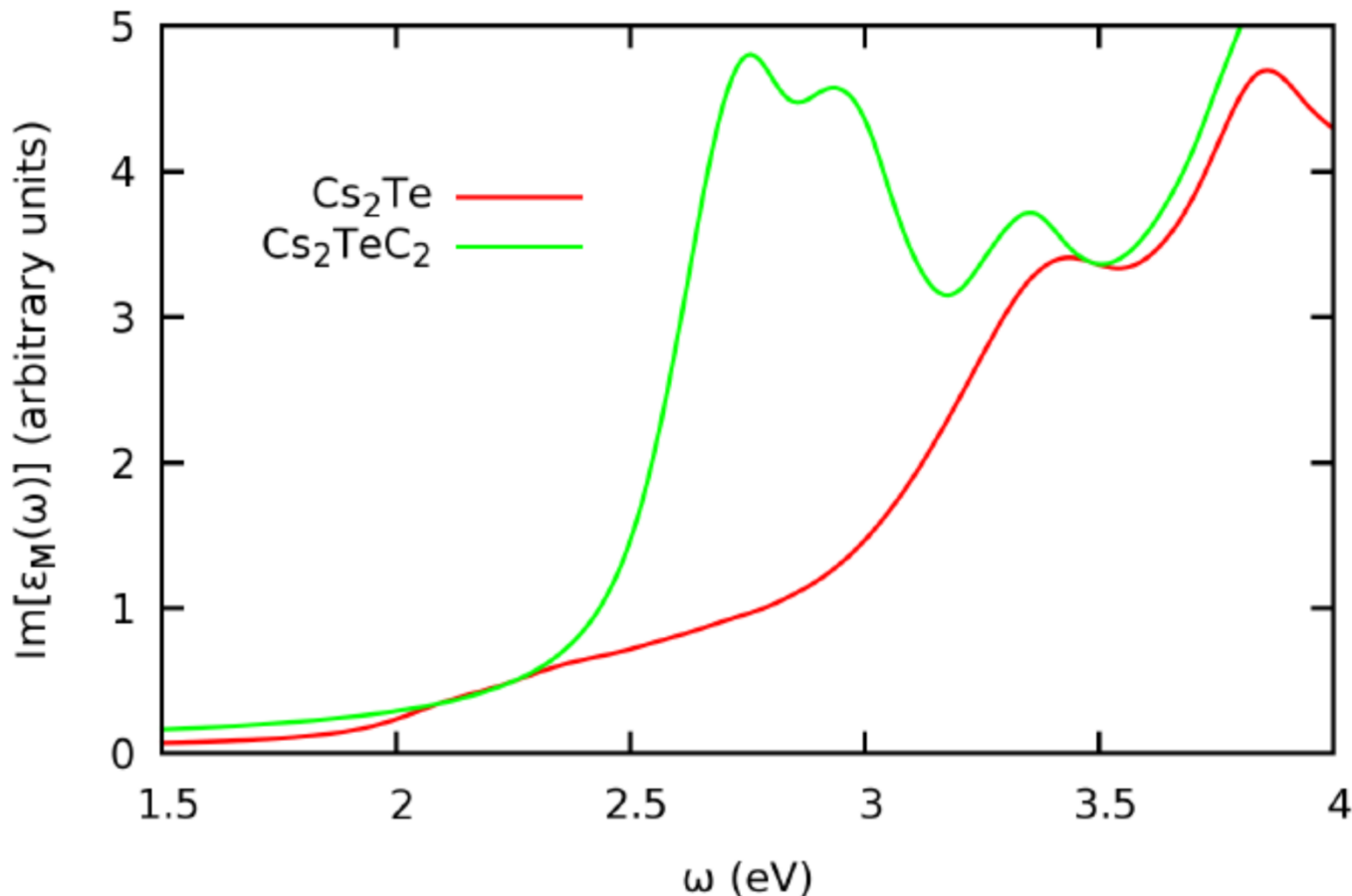
- Electronic band structure calculations, using PBE exchange-correlation functional, for bulk Cs_2Te and Cs_2TeC_2 . Note flat bands characteristic of high density of states, also seen in all ternary acetylides studied to date.
- The PBE functional tends to underestimate the energy gap by about 1 eV, but the work function and DOS are consistent with experimental data for Cs_2Te .

Density of states (DOS): Comparison of Cs_2Te and Cs_2TeC_2



J.Z. Terdik, K. Nemeth

Comparison of optical absorption spectra



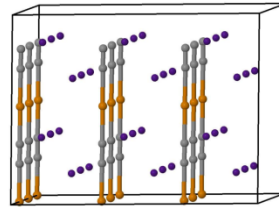
Optical absorption spectrum is the imaginary part of the dielectric constant.

QE of Cs_2TeC_2 expected to be comparable to Cs_2Te .

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

Calculated surface properties (DFT), no surface relaxation

- Significant ϕ anisotropy among rod-perpendicular (001) and rod-parallel, (110) and (010), orientations.
- (010) surfaces are the most stable and show the lowest work functions.
- Approx. 1-2 eV reduction in the work function between (001) and (010) surfaces.
- Changing alkali atom has effect on work function and bandgaps.
- Rod-perpendicular surface could behave like a 2D nanotip array.



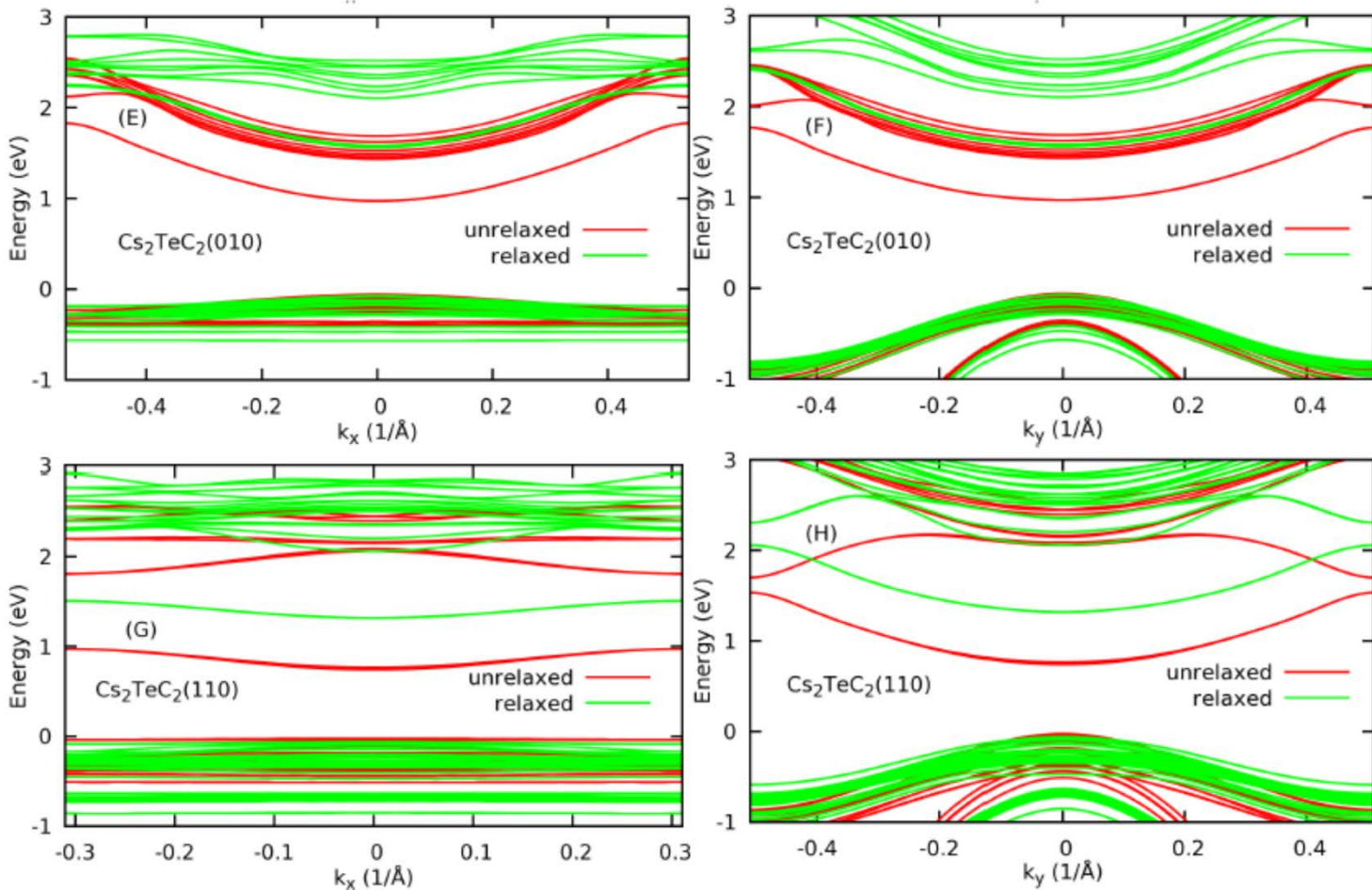
Compound and surface	unrelaxed		
	Φ (eV)	$E_g(\Gamma)$ (eV)	σ (eV/Å ²)
o-Cs ₂ C ₂ (010)	2.80	1.25	0.023
h-Cs ₂ C ₂ (001)	2.56	1.14	0.027
Na ₂ PdC ₂ (001)	3.58	1.13	0.067
Na ₂ PdC ₂ (110)	3.73	1.65	0.029
Na ₂ PdC ₂ (010)	2.65	1.91	0.019
Cs ₂ PdC ₂ (001)	2.90	1.43	0.046
Cs ₂ PdC ₂ (110)	2.73	0.88	0.026
Cs ₂ PdC ₂ (010)	1.33	0.78	0.015
Na ₂ TeC ₂ (001)	3.40	1.03	0.029
Na ₂ TeC ₂ (110)	3.80	0.91	0.025
Na ₂ TeC ₂ (010)	2.75	1.43	0.015
Cs ₂ TeC ₂ (001)	3.71	1.86	0.022
Cs ₂ TeC ₂ (110)	2.77	0.77	0.020
Cs ₂ TeC ₂ (010)	1.71	1.00	0.013

Effect of surface relaxation

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

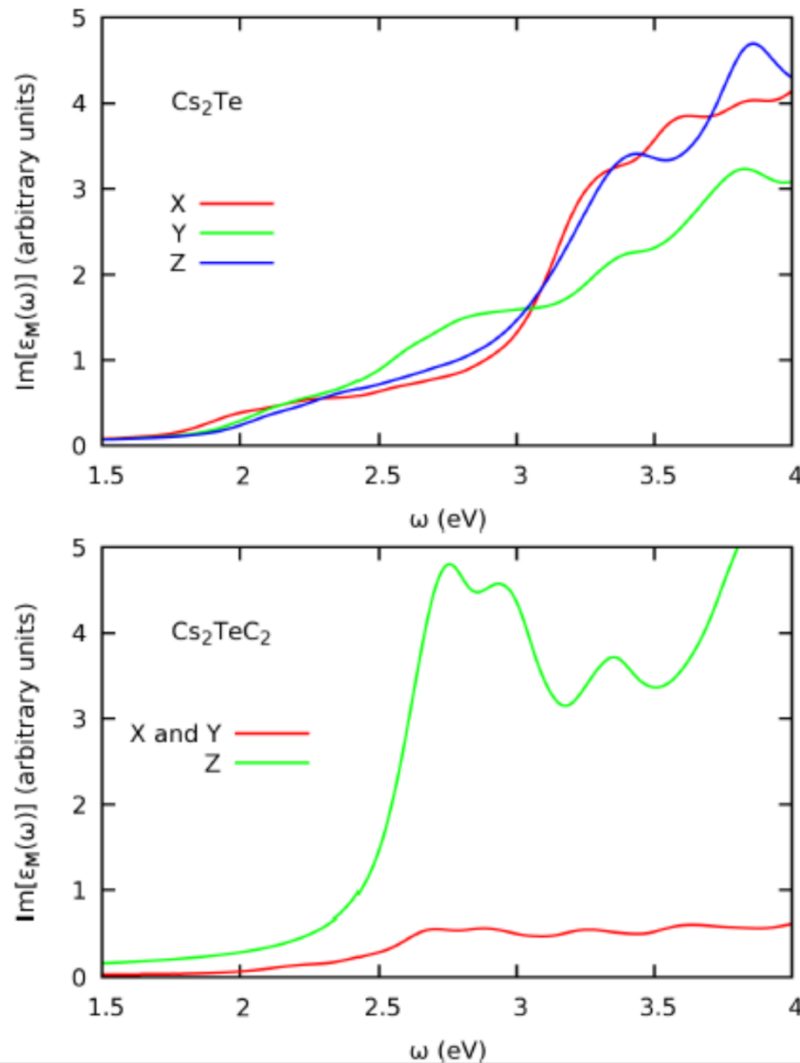
- Surface relaxations increase the work-function but maintain a >1eV reduction compared to expt and simulated workfunctions of cesium telluride
- The per atom change in energy for surface relaxation is comparable to thermal energy indicating both relaxed and unrelaxed geometries contribute to observed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

Effect of surface relaxation on band structure



Electronic bands of surfaces with surface parallel 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 .

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 **parallel** (bottom, green) to the rods. No comparably large anisotropy is observed in cesium telluride.

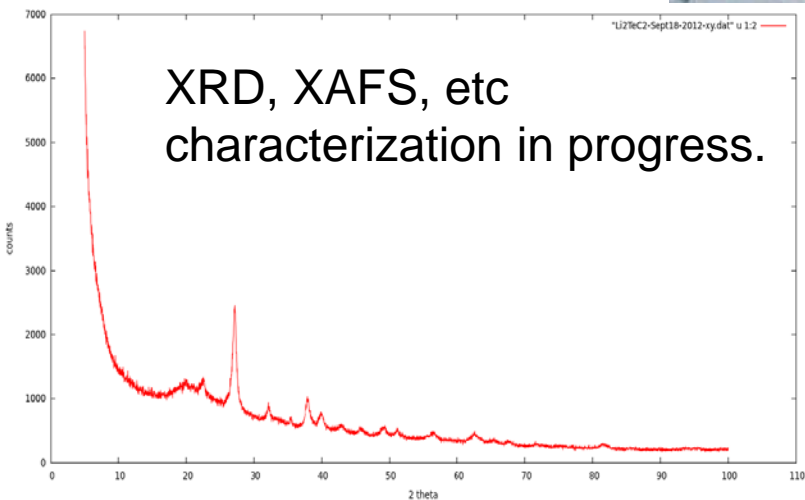
Status of Synthesis

So far, reaction of A_2Te tellurides with acetylene (C_2H_2) gas in suitable organic solvents seems most promising.

Best synthetic material so far for Li_2TeC_2 .



XRD, XAFS, etc
characterization in progress.



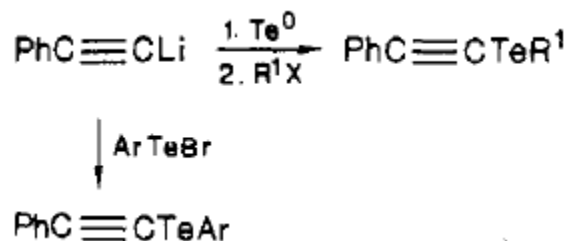
Chemical Reactivity of Tellurides

- Regarding degradation of photocathode in imperfect vacuum; Cs_2Te oxidizes to Cs_2O and Cs-polytellurides Cs_2Te_n ($n > 1$, purple color) :



[D.M. Smith, J.A. Ibers, "Syntheses and solid-state structural chemistry of polytelluride anions", Coordination Chemistry Reviews, 200–202 (2000) 187–205]

- Cs_2TeC_2 has no telluride (Te^{2-}) ion; Te's oxidation number is zero. No reactivity to oxygen is expected, as Te^0 cannot give away electrons, as opposed to Te^{2-} ion.
- Acetylenic tellurides ($\text{R-C}\equiv\text{C-Te-R}'$) have been studied in organometallic chemistry:



[M.J. Dubdoub, J.V. Comasseto, "Acetylenic Tellurides: Synthesis and Reactivity", Organometallics (1988), 7, 84-87.]

- Cs_2PdC_2 and other A_2MC_2 have been synthesized [U. Ruschewitz et al.]

Summary

- Ultra-bright photocathodes are a key technology for future light sources.
- We have investigated ideas using intuition and DFT to tune photocathode properties to enhance future light source performance.
- “Designer” acetylated $\text{Cs}_2\text{Te} - \text{Cs}_2\text{TeC}_2$ – and other systems in this class are predicted to have low work functions. The QE of Cs_2TeC_2 is predicted to be comparable to Cs_2Te . The rod-perpendicular orientation may exhibit low emittance. Robustness in imperfect vacuum also predicted.
- Preliminary synthesis is ongoing through collaboration at IIT/ANL; results are encouraging.
- Characterization using surface science techniques is planned at APS and IIT; also, expression of interest to use LBNL/ALS beamline ARPES system.
- Characterization in a gun of promising cathodes is desired; expression of interest in collaboration at several labs (year(s) away).
- Funding challenges; progress is proportional to funding.

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 Cs₂C₂ are denoted as o-Cs₂C₂ and h-Cs₂C₂, 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			DFT		
	a	b	c	a	b	c
Cs (Im $\bar{3}m$)[13]	6.067	6.067	6.067	6.067	6.067	6.067
Te (P3 ₁ 21) [14]	4.526	4.526	5.920	4.458	4.458	5.925
Cs ₂ Te (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 ₂ C ₂ (I4 ₁ /acd)[17]	6.778	6.778	12.740	6.941	6.941	13.027
o-Cs ₂ C ₂ (Pnma)[18]	9.545	5.001	10.374	9.826	5.061	10.491
h-Cs ₂ C ₂ (P $\bar{6}2m$)[18]	8.637	8.637	5.574	8.728	8.728	6.048
CsAgC ₂ (P4 ₂ mmc)[6]	5.247	5.247	8.528	5.317	5.317	9.036
Na ₂ PdC ₂ (P $\bar{3}m1$)[5]	4.464	4.464	5.266	4.632	4.632	5.284
Cs ₂ PdC ₂ (P $\bar{3}m1$)[4]	5.624	5.624	5.298	5.804	5.804	5.265
Na ₂ TeC ₂ (P $\bar{3}m1$)	-	-	-	4.767	4.767	6.102
Cs ₂ TeC ₂ (P $\bar{3}m1$)	-	-	-	5.820	5.820	6.152

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Phys. Rev. B 86, 035142 (2012).

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)		d(M-C) (Å)	
	EXPT	DFT	EXPT	DFT
C (Fd $\bar{3}m$)[16]	1.544	1.547	-	-
C ₂ H ₂ (gas) [19]	1.203	1.203	-	-
Na ₂ C ₂ (I4 ₁ /acd) [17]	1.204	1.261	-	-
o-Cs ₂ C ₂ (Pnma) [18]	1.385	1.269	-	-
h-Cs ₂ C ₂ (P $\bar{6}2m$)[18]	0.934	1.267	-	-
CsAgC ₂ (P4 ₂ mmc) [6]	1.216	1.249	2.016	2.034
Na ₂ PdC ₂ (P $\bar{3}m1$) [5]	1.262	1.271	2.019	2.006
Cs ₂ PdC ₂ (P $\bar{3}m1$) [4]	1.260	1.280	2.019	1.993
Na ₂ TeC ₂ (P $\bar{3}m1$)	-	1.259	-	2.422
Cs ₂ TeC 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)		$E_g(\Gamma)$ (eV)	σ (eV/Å ²)
	EXPT	DFT	DFT	DFT
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K ₂ CsSb	1.9-2.1 [23, 24]	-	-	-