Anomalous Workfunction Anisotropy in Ternary Acetylides

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Anomalous anisotropy of workfunction values in ternary alkali metal transition metal acetylides is reported. Workfunction values of some characteristic surfaces in these emerging semiconducting materials may differ by more than \( \approx 2 \) eV as predicted by Density Functional Theory calculations. This large anisotropy is a consequence of the relative orientation of rod-like \([MC_2]_\infty\) negatively charged polymeric subunits and the surfaces, with \( M \) being a transition metal or metalloid element and \( C_2 \) refers to the acetylide ion \( C_2^- \), with the rods embedded into an alkali cation matrix. It is shown that the conversion of the seasoned \( \text{Cs}_2\text{Te} \) photo-emissive material to ternary acetylide \( \text{Cs}_2\text{TeC}_2 \) results in substantial reduction of its \( \approx 3 \) eV workfunction down to 1.71-2.44 eV on the \( \text{Cs}_2\text{TeC}_2(010) \) surface while its high quantum yield is preserved. Similar low workfunction values are predicted for other ternary acetylides as well, allowing for a broad range of applications from improved electron- and light-sources to solar cells, field emission displays, detectors and scanners.

I. INTRODUCTION

For many photo-physical applications photoemissive materials are sought after that can turn a high fraction of the incident photons into emitted electrons, i.e. materials that have a high quantum-yield. Often, the quantum-yield of these materials depends heavily on the wavelength of incident photons. For many applications, ranging from electron-guns for synchrotrons and free-electron lasers to night vision devices, high quantum-yield photoemission using visible or infrared irradiation is desirable. In electron-guns of synchrotrons and free-electron lasers, emission in the visible range is advantageous for improved control of the shape of the emitted electron bunch that is critical for time-resolved applications. In night-vision devices a very low flux of infrared photons has to be turned into emitted electrons with a high yield in order to obtain an image as sharp as possible. Therefore there is a quest for new and improved materials with optimized quantum-yield and low-workfunction.\(^{[4]}\)

\( \text{Cs}_2\text{Te} \) has been known since the 1950-s for its high quantum-yield\(^{[5]}\) using ultraviolet illumination with photon-energies above \( \approx 3.0 \) eV and has been used for many decades as a primary high-yield photocathode. Besides not being photoemissive in the visible region, its other main drawback is that its surface gets oxidized in practical vacuum whereby its quantum efficiency substantially reduces\(^{[6]}\). Despite this disadvantage, \( \text{Cs}_2\text{Te} \) still has 20-30 times longer operational lifetime than competing multi-alkali antimonide photocathodes, such as \( \text{K}_2\text{CsSb} \) and \( \text{(Cs)Na}_3\text{KSB} \), especially when operated in radio-frequency accelerating cavities\(^{[3]}\).

In the process of attempting to design modifications of \( \text{Cs}_2\text{Te} \) with lowered workfunction and preserved high quantum-yield we have considered the effects of small gas molecules on \( \text{Cs}_2\text{Te} \) surfaces. Such effects have been studied by di Bona \textit{et al.}\(^{[8]}\) using small gas molecules occurring in vacuum, such as \( \text{O}_2, \text{N}_2, \text{CO}_2, \text{CO} \) and \( \text{CH}_4 \). It occurred to us that the effect of another small gas molecule, acetylene \( (\text{C}_2\text{H}_2) \) has not been considered yet, despite the potentially interesting reactions between \( \text{C}_2\text{H}_2 \) and \( \text{Cs}_2\text{Te} \). \( \text{C}_2\text{H}_2 \) is widely used for welding (not in accelerators though) and it might occur in accelerator-vacuums as well, in trace amounts. It is an acidic compound and prefers to decompose to acetylide anion \( \text{C}_2^- \) and to \( 2\text{H}^+ \) in the presence of a base. Based on the acidic character of \( \text{C}_2\text{H}_2 \), one might investigate the working hypothesis that the reaction of

\[
\text{Cs}_2\text{Te}(cr) + \text{C}_2\text{H}_2(g) \rightarrow \text{Cs}_2\text{TeC}_2(cr) + \text{H}_2(g)
\]

would produce a ternary acetylide \( \text{Cs}_2\text{TeC}_2 \) whereby the oxidation number of \( \text{Te} \) would change from -2 to 0 and that of \( \text{H} \) from +1 to 0, with \( \text{(cr)} \) denoting crystal and \( \text{(g)} \) gas phase. Interestingly, the class of ternary \( \text{(i.e. three-component)} \) acetylides indeed exists, involving already synthesized members with the general formula of \( \text{A}_2\text{MC}_2 \)

![FIG. 1: A side-view of the 3x3x2 supercell of the hexagonal unit cell of \( \text{Cs}_2\text{TeC}_2 \). Bronze spheres denote Te, grey ones C, dark-purple ones Cs. Notice the \([\text{TeC}_2]_\infty\) rods.](image-url)
with A∈[Na,K,Rb,Cs] and M∈[Pd,Pt], and the oxidation number of the metal M in them is zero. All existing compounds of the $A_2MC_2$ formula have a hexagonal unit cell with rod-like $[MC_2]_\infty$ substructures running parallel with the main crystallographic axis, and very similar distribution of alkali atoms around the $[MC_2]_\infty$ rods, just as indicated in Figs. 1 and 2. All known $A_2MC_2$ materials are colored semiconductors with 2.1-2.8 eV direct band gaps of some ternary acetylides and CsTe (Fig. 5), as shown in Fig. 3. The overall characteristics of these bands is similar to that calculated previously for ternary acetylides, e.g. in Refs. 5, 7 and 11. Band gaps of bulk CsTe, Cs$_2$TeC$_2$ and NaTeC$_2$ have been predicted to be between 1.8-2.0 eV, using the PBE functional (Fig. 4).

We have also calculated the optical absorption spectra of some ternary acetylides and CsTe (Figs. 3 and 4) in the Random Phase Approximation (RPA) using the YAMBO-code. All optical absorption calculations have been performed with a resolution of $\Delta k < 0.1 \text{ Å}^{-1}$, and a Gaussian broadening of 0.03 Ry. Note that for maximum absorption the polarization of the light was parallel with rods in the ternary acetylides and parallel with the crystallographic c-axis in Cs$_2$Te (Fig. 7). Due to the lack of norm-conserving pseudopotential for Pd, optical absorption spectra of Na$_2$PdC$_2$ and Cs$_2$PdC$_2$ could not be calculated. In order to associate these gaps with transition probabilities, a crude approximation of these spectra using only plane waves with G=0 wave-vectors was attempted. It indicates absorption maxima at 1.8 and 2.6 eV for Na$_2$PdC$_2$ and Cs$_2$PdC$_2$, respectively (Fig. 3). Unexpectedly, PBE calculations at the same geometries result in about 1.0 eV larger gaps than the experimental ones.

III. RESULTS AND DISCUSSION

The optimization reveals that Cs$_2$TeC$_2$ has a very similar structure to other compounds of the $A_2MC_2$ class. Our DFT calculations predict that the electronic energy change in Eq. 1 is $\Delta E = +1.1$ eV per Cs$_2$TeC$_2$ unit, while that in the alternative reaction of

$$\text{Cs}_2\text{C}_2(\text{cr}) + \text{Te(cr)} \rightarrow \text{Cs}_2\text{TeC}_2(\text{cr}) \quad (2)$$

[FIG. 2: A top-down view of a 3x3x2 supercell of the hexagonal unit cell of Cs$_2$TeC$_2$. Color codes are identical with those in Fig. 1. The [TeC$_2$]$_\infty$ rod-like 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.]
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 |
|----------------------------------|-------------------------|------|-----|
| Cs(Im3m)                        | 6.067 6.067 6.067 6.067 6.067 |      |     |
| Te(P3121)                        | 4.526 4.526 5.920 4.458 4.458 5.925 |      |     |
| Cs2Te(Pnma)                      | 9.512 5.838 11.748 9.558 5.832 11.750 |      |     |
| C(Fd3m)                          | 3.567 3.567 3.567 3.573 3.573 3.573 |      |     |
| Na2C2(I41/acd)                   | 6.778 6.778 12.740 6.941 6.941 13.027 |      |     |
| o-Cs2C2(Pnma)                    | 9.545 5.001 10.374 9.826 5.061 10.491 |      |     |
| h-Cs2C2(P6222)                   | 8.637 8.637 5.374 8.728 8.728 6.048 |      |     |
| CsAgC2(P4emmc)                   | 5.247 5.247 8.528 5.317 5.317 9.036 |      |     |
| Na2PdC2(Pmm)                     | 4.464 4.464 5.266 4.632 4.632 5.284 |      |     |
| Cs2PdC2(Pmm)                     | 5.624 5.624 5.298 5.804 5.804 5.265 |      |     |
| Na2TeC2(P3m1)                    | - - - 4.767 4.767 6.102 |      |     |
| Cs2TeC2(P3m1)                    | - - - 5.820 5.820 6.152 |      |     |

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

| Compound, Space-group & ref. | d(C-C) (Å) | d(M-C) (Å) | EXPT | DFT | EXPT | DFT |
|------------------------------|-------------|-------------|------|-----|------|-----|
| C(Fd3m)                      | 1.544 1.547 | - -         |      |     |      |     |
| C2H2(gas)                    | 1.203       | 1.203       |      |     |      |     |
| Na2C2(I41/acd)               | 1.204 1.261 | - -         |      |     |      |     |
| o-Cs2C2(Pnma)                | 1.385 1.269 | - -         |      |     |      |     |
| h-Cs2C2(P6222)               | 0.934 1.267 | - -         |      |     |      |     |
| CsAgC2(P4emmc)               | 1.216       | 1.249 2.016 2.034 |      |     |      |     |
| Na2PdC2(P3m1)                | 1.262 1.271 2.019 2.006 |     |     |
| Cs2PdC2(P3m1)                | 1.260 1.280 2.019 1.993 |     |     |
| Na2TeC2(P3m1)                | - 1.259    2.422 |      |     |
| Cs2TeC2(P3m1)                | - 1.257    2.452 |      |     |

is ΔE = -0.95 eV, indicating the stability of the Cs2TeC2 crystal and an alternative synthesis route. In fact the synthesis in Eq. 2 is analogous to that of already existing A2MC2 compounds. The predicted stability of a ternary acetylide with metalloid element (Te) instead of metalloids, while preserving the peculiar rod-like substructures. Our analysis at this point cannot exclude the existence of other structures for Cs2TeC2. We have attempted to start the optimization of a 5 atomic unit cell of Cs2TeC2 from several randomly chosen initial lattice parameters and atomic positions. In all cases the formation of [TeC2]∞ rods was evident after a few hundred steps. Here we have relied on the fact that A2MC2 compounds have been found only with hexagonal rod packing so far. Also, the structure of h-Cs2C2 already contains the hexagonal rod-packing of the C2 unit leaving place for intercalatable atoms, such as Te, or transition metals, between neighboring C2-s along a rod.

One should also note that the linear chains of carbon atoms, [C2]∞ with alternating C-C and C≡C bonds (polycarbonye) or with uniform C≡C bonds (cumulenes, polyallenes), have long been a subject of theoretical and materials science interest. However, unlike their hydrogenated analogue, [C2H2]∞ polycetylene, containing alternating C-C and C≡C bonds, famous for high electrical conductivity on the order of that of silver when doped, [C2]∞ could not have been synthesized until a decade ago, proving the existence of [C2]n with n≥200,300. Interestingly, the efficient synthesis of [C2]n involves copper-acetylide. Furthermore, copper-

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| Compound | Φ (eV) | E₀(Γ) (eV) | σ (eV/A²) | EXPT | DFT | DFT | DFT |
|----------|--------|------------|-----------|------|-----|-----|-----|
| Cs(100)  | 2.14²³ | 2.00       | 0.29      | 0.005 |     |     |     |
| Te(001)  | 4.9²⁴   | 5.02       | 0.54      | 0.036 |     |     |     |
| Cs2Te(001) | 2.90-3.0²⁴ | 3.08   | 0.77      | 0.015 |     |     |     |
| Cs2Te(010) | 2.90-3.0²⁴ | 2.90   | 1.04      | 0.014 |     |     |     |
| (Cs)Na3KSB | 1.54²³ | -         | -         |     |     |     |     |
| K₂CsSB   | 1.9-2.1²³ | -         | -         |     |     |     |     |

TABLE III: Experimental and calculated (DFT) properties of photoemissive surfaces of validation materials: workfunctions (Φ), bandgaps at the Γ-point E₀(Γ) and surface energies (σ).

| Compound | Φ (eV) | E₀(Γ) (eV) | σ (eV/A²) | EXPT | DFT | DFT | DFT |
|----------|--------|------------|-----------|------|-----|-----|-----|
| o-Cs2C2(010) | 2.80 | 1.25       | 0.023     | -    | -   | -   | -   |
| h-Cs2C2(001) | 2.56 | 1.14       | 0.027     | -    | -   | -   | -   |
| Na2PdC2(001) | 3.58 | 1.13       | 0.067     | -    | -   | -   | -   |
| Na2PdC2(110) | 3.73 | 1.65       | 0.029     | 4.17 | 2.34 | 0.024 |     |
| Na2PdC2(010) | 2.65 | 1.91       | 0.019     | 2.68 | 2.45 | 0.017 |     |
| Cs2PdC2(001) | 2.90 | 1.43       | 0.046     | -    | -   | -   | -   |
| Cs2PdC2(110) | 2.73 | 0.88       | 0.026     | 2.73 | 1.16 | 0.022 |     |
| Cs2PdC2(010) | 1.33 | 0.78       | 0.015     | 2.03 | 1.74 | 0.013 |     |
| Na2TeC2(001) | 3.40 | 1.03       | 0.029     | -    | -   | -   | -   |
| Na2TeC2(110) | 3.80 | 0.91       | 0.025     | 4.67 | 2.04 | 0.009 |     |
| Na2TeC2(010) | 2.75 | 1.43       | 0.015     | 2.68 | 1.34 | 0.015 |     |
| Cs2TeC2(001) | 3.71 | 1.86       | 0.022     | -    | -   | -   | -   |
| Cs2TeC2(110) | 2.77 | 0.77       | 0.020     | 2.98 | 1.38 | 0.019 |     |
| Cs2TeC2(010) | 1.71 | 1.00       | 0.013     | 2.44 | 1.63 | 0.009 |     |

TABLE IV: Calculated (DFT) properties of photoemissive surfaces of acetylide compounds: workfunctions (Φ), bandgaps at the Γ-point E₀(Γ) and surface energies (σ). Relaxed slabs refer to the relaxation of unrelaxed ones with the central 2 layers fixed. For h-Cs2C2(001) and Na2TeC2(010), E₀(Γ) ≈ 0.05 eV has been found for a single band above E_F as well.
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FIG. 3: Bandstructures of Na$_2$PdC$_2$ and Cs$_2$PdC$_2$ using the PBE exchange-correlation functional. The k-space was 14×14×14 large. The Fermi energy is at 0 eV. Flat bands are characteristic for ternary acetylides.

Acetylides can also be used as the starting material for their synthesis, pointing to the intimate relationship of the rod-like [MC$_2$]$_\infty$ substructures in ternary acetylides A$_2$MC$_2$ and AMC$_2$ to linear carbon chains. Copper-acetylide molecules are also studied for their self assembly into extremely thin nanowires. It is also important to note that while transition-metal acetylides are known explosives, their alkalinated versions AMC$_2$ and A$_2$MC$_2$ are not explosive at all and can survive heating up to ≈500-600 °C and grinding.

As it is indicated in Table IV, the workfunctions of different surfaces of Cs$_2$TeC$_2$ have largely different values. Concerning the three most important surfaces (Fig. 2), there is a ≈1 eV decrease as one goes from (001) through (110) to (010) in each step, with workfunctions of 3.71, 2.77 and 1.71 eV, and surface energies of 0.022, 0.020 and 0.013 eV/Å$^2$, respectively, for the unrelaxed surfaces. Relaxed surfaces have somewhat greater workfunction values, but still allowing for emission in the visible spectrum. Relaxation of the surface layers greatly influences the unoccupied bands, while the occupied ones change significantly less, as indicated in Fig. 8. Also note that the total energy differences between relaxed and unrelaxed surfaces are small, for example they are only 0.3 eV for a whole Cs$_2$TeC$_2$(010) slab, i.e. about 0.01 eV/atom in the top surface layers which allows for thermal population of a great variety of surface structures at room temperature. In Cs$_2$TeC$_2$(010) and Na$_2$TeC$_2$(010) surface relaxations may break the [TeC$_2$]$_\infty$ rods, while the rods stay intact in Pd (or other transition metal) based ternary acetylides. In Cs$_2$PdC$_2$(010) and Na$_2$PdC$_2$(010) the rods provide quasi rails along which Cs-s and Na-s can easily move due to thermal motion. This is also in accordance with the anomalous broadening of peaks in the x-ray powder spectra of ternary acetylides. Such an
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anomalous anisotropy of workfunction values is highly unusual and represents a broad range of workfunction choice within a single material, allowing for emission in ultraviolet, visible and near infrared radiation. The lowest surface cleavage energy Cs$_2$TeC$_2$ surface, (010), has a similar surface energy as those of Cs$_2$Te surfaces; it is, however, associated with a much lower (by $\approx 1.3$ eV) workfunction. The highly anisotropic properties of Cs$_2$TeC$_2$ are due to the relative orientation of the rod-like [TeC$_2$]$\infty$ substructures and the surfaces. Surface energies reveal that cutting the rods by cleaving the M-C bonds ([001] surface) is energetically disadvantageous, and it is also disadvantageous to allow for rods to be directly exposed on the surface ([110] surface), while cleavage between Cs atoms with rods embedded under the surface is the most energetically favorable construct ([010] surface). While numerous variants of surface coverages may exist at different temperatures that expose or cover rods by Cs on the surface, here we do not go beyond a single surface unit to study the energetics of surfaces. The sticking of Cs to these surfaces may be a similarly important issue here as in the case of cesiated III/V semiconductor surfaces (e.g. GaAs)$^{123}$ As the rods are twice negatively charged per MC$_2$ unit, we expect that the sticking of Cs cations would be relatively strong.

High anisotropy can be observed in Na$_2$PdC$_2$, Na$_2$TeC$_2$ and Cs$_2$PdC$_2$ as well, with somewhat smaller, 1.1-1.6 eV difference between the extremal surfaces. The type of the alkali atom very sensitively influences the workfunctions: substituting Na with Cs results in more than 1 eV reduction of the workfunction on the (110) and (010) surfaces independently from the type of the [MC$_2$]$\infty$ chain, even though the M-C bonding in these chains is very different. One has to note that the Pd-C distance is significantly shorter than the Te-C in these compounds, 2.01 Å vs. 2.45 Å, respectively, while Te and Pd have very similar covalent radii of $\approx 1.4$ Å.$^{139}$ The (001) surface energies also indicate a much stronger Pd-C bond than Te-C one. While there is a $\sigma$-bond in both Pd-C and Te-C links between the 2sp$_1$ hybrid orbital of the C atom and the 5sp$_1$ hybrids of Pd and Te (all oriented along the M-C-C line) the Pd-C link is further strengthened by strong back-donation of Pd 4d shell electrons to the antibonding $\pi$-orbitals of the C$^{2-}$ ions, also associated with lengthening of the C-C bond.$^{38}$ Also note that Cs$_2$Te (and also Cs$_2$TeC$_2$) has the advantage over the formerly mentioned multi-alkali-antimonides that Cs is better bound in them allowing for longer operational lifetime.$^{41}$ Another interesting comparison can be made to amorphous cesiated carbon films obtained from the co-deposition of high-energy negatively charged carbon ions and Cs on silicon substrates, as the low, $\approx 1.1$ eV workfunction in them might be associated with increased acetylide ion concentration. However, there is no available data of how well Cs is bound in these systems.$^{38}$

In order to estimate the quantum-yield of Cs$_2$TeC$_2$ relative to Cs$_2$Te, we have calculated their optical absorption spectra (Fig. 6) using the lowest energy 4000 planewaves at which the spectrum becomes saturated against further increase of the number of planewaves. The spectra indicate that acetylation of Cs$_2$Te shifts its first absorption peak in the visible region to 2.7 eV, while preserving the same absorption intensity. This comparison suggests that Cs$_2$TeC$_2$ may have similarly high quantum efficiency as that of Cs$_2$Te, however, even for visible and potentially also for near infrared photons. The bandgaps at the $\Gamma$ point of Cs$_2$TeC$_2$ surfaces (see Table IV) also support that photon-energies near the workfunction are sufficient to induce emission in this mater-
FIG. 7: Dependence of the optical absorption spectra of bulk Cs$_2$Te and Cs$_2$TeC$_2$ on the polarization of the incident light. The z-direction is along the main crystallographic axis (c-axis), which is parallel with the [TeC$_2$]$_\infty$ chains in Cs$_2$TeC$_2$. While absorption in Cs$_2$TeC$_2$ is highly anisotropic, with $\approx 9$ times higher values for the z-direction than for the x and y ones, there is no significant anisotropy of absorption in Cs$_2$Te. Similar anisotropy can be seen in Na$_2$TeC$_2$ as well, and likely in all ternary acetylides, due to the electric dipoles along the [MC$_2$]$_\infty$ chains.

An interesting characteristics of ternary acetylides is the extensive presence of flat bands (see Figs. 3 and 4). While there are some flat band parts in Cs$_2$Te as well, such a feature is much more characteristic for ternary acetylides. Flat bands greatly increase the density of states for some spectral regions thus they contribute to increased absorption of light. Interestingly, not only the workfunctions of these materials show high anisotropy, but also their optical absorption (see Fig. 2). The optical absorption is almost a magnitude greater when the light’s polarization vector is parallel with the [MC$_2$]$_\infty$ rods. This property can allow for example for the generation of pulsed electron beams when these surfaces are illuminated by circularly polarized light. Several other optical applications can be envisioned based on the anisotropy of optical absorption in ternary acetylides, such as polarizers and optical switching elements.

It is also important to call attention to the rest of the ternary acetylides as valuable photoemissive materials. For example the already synthesized Cs$_2$PdC$_2$(010) material is predicted here to have a very low 1.33-2.03 eV workfunction even smaller than that of Cs$_2$TeC$_2$(010) and a similar density of states.

V. CONCLUSIONS

In the present work we have demonstrated unique photoemissive properties of ternary acetylides, such as low workfunctions, high workfunction and optical absorption anisotropy and high quantum yield. We have also demonstrated how the acetylation of the seasoned Cs$_2$Te photocathode material leads to significantly lowered workfunction while preserving its high quantum yield.

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FIG. 8: Electronic bands of the slabs of the (010) and (110) surfaces of Cs$_2$PdC$_2$ and Cs$_2$TeC$_2$ along the two orthogonal reciprocal surface lattice vectors $k_x$ (panels A, C, E and G) and $k_y$ (panels B, D, F and H). The [MC$_2$]$_\infty$ rods are parallel with the y direction for all (010) and (110) surface slabs. Bands at both relaxed (green) and unrelaxed (red) slabs are shown. The Fermi energy is at 0.
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