Searching for low-workfunction phases in the Cs-Te system: the case of Cs$_2$Te$_5$

Anthony Ruth$^{1}$, Károly Németh$^{1,2,*}$, Katherine C. Harlay$^2$, Joseph Z. Terdik$^2$, Jeff Terry$^1$, Linda Spentzouris$^{1,2}$

$^1$Physics Department, Illinois Institute of Technology, Chicago, IL 60616 USA and
$^2$Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

(Dated: February 6, 2014)

We have computationally explored workfunction values of Cs$_2$Te$_5$, an existing crystalline phase of the Cs-Te system and a small bandgap semiconductor, in order to search for reduced workfunction analogues of Cs$_2$Te that preserve the exceptionally high quantum efficiency of the Cs$_2$Te seasoned photoemissive material. We have found that the Cs$_2$Te$_5$(010) surface exhibits a workfunction value of $\approx 1.9$ eV when it is covered by Cs atoms. Cs$_2$Te$_5$ is analogous to our recently proposed low-workfunction materials, Cs$_2$TeC$_2$ and other ternary acetylides [J. Z. Terdik, et al., Phys. Rev. B 86, 035142 (2012)], in as much as it also contains quasi one-dimensional substructures embedded in a Cs-matrix, forming the foundation for anomalous workfunction anisotropy, and low workfunction values. The one-dimensional substructures in Cs$_2$Te$_5$ are polytelluride ions in a tetragonal rod packing. Cs$_2$Te$_5$ has the advantage of simpler composition and availability as compared to Cs$_2$TeC$_2$, however its low workfunction surface is less energetically favored to the other surfaces than in Cs$_2$TeC$_2$.

I. INTRODUCTION

Cesium Telluride (Cs$_2$Te) has been known since the 1950-s as an exceptionally high quantum efficiency photoemissive material$^{[1]}$ it can turn as much as $\approx 20\%$ of the incident ultraviolet photons into emitted electrons.$^{[2]}$ Cesium Telluride also has the advantage of relatively long operational lifetime, 20-30 times longer than that of competing multi-alkali antimonide photocathodes, such as K$_2$CsSb and (Cs)Na$_3$Ksb. While K$_2$CsSb and (Cs)Na$_3$Ksb require ultrahigh vacuum for operation, Cs$_2$Te can operate in orders of magnitude lower levels of vacuum$^{[3]}$. In order to further enhance the photoemissive properties of Cs$_2$Te for certain applications, modifications are required that decrease its workfunction from the $\approx 3.0$ eV down to the visible light spectrum (1.5-3.0 eV) while preserving its high quantum efficiency. Such modifications can lead to, for example, for high brightness electron gun$^{[4]}$, better pulse shaping of the incident photons in the visible spectrum and eliminating the need for wavelength down-conversion. Wavelength down-conversion is used to convert the typically near-infrared photons of the laser source to ultraviolet wavelength which causes a great loss of the intensity of the initial laser-beam. One possible way to an improved photoemissive material that we recently proposed$^{[5]}$ is the acetylation of Cs$_2$Te leading to Cs$_2$TeC$_2$, a new member of the existing family of ternary acetylidy$^{[6,7]}$ compounds. Electronic structure calculations predict that the new Cs$_2$TeC$_2$ and other, existing ternary acetylides, such as Cs$_2$PdC$_2$ would have similarly high quantum efficiencies as Cs$_2$Te, but significantly lower, 2.0-2.4 eV workfunctions.

An alternative route to the acetylation in developing improved photoemissive analogues/derivatives of Cs$_2$Te might be in the exploration of photoemissive properties of other Cs-Te phases. A comprehensive review of alkali tellurides by D. M. Smith and J. A. Ibers$^{[8]}$ called our attention to Cs$_2$Te$_5$, an existing$^{[9]}$ crystalline phase of Cs and Te. Remarkably, the Te$_5^{2-}$ polytelluride anions in Cs$_2$Te$_5$ self organize to $\approx 4$ Å wide wavy ribbons of Te with continuous covalent Te-Te networks, which are embedded into a Cs matrix, such as shown in Fig. 1. In the wavy Te-ribbons, six-membered rings of Te in chair-conformation are connected via common vortices into quasi 1D chains, as depicted in Fig. 2. These quasi 1D substructures of Cs$_2$Te$_5$ resemble the rod-like polymeric [-Te-C≡C]-$_n$ substructures that are responsible for the improved photoemissive properties of Cs$_2$TeC$_2$. This structural analogy directed our attention towards the computational analysis of Cs$_2$Te$_5$ to check whether it can potentially serve as an improvement to Cs$_2$Te and ternary acetylides.

II. METHODOLOGY

The electronic structure calculations in the present study have been carried out using the Quantum Espresso program package$^{[11]}$. The PBE exchange-correlation potential$^{[12]}$ has been used with norm-conserving Cs and Te pseudopotentials identical to those in our study for Cs$_2$TeC$_2$ in Ref. 5. The wavefunction-cutoff was 80 Rydbergs. The k-space grids were at least $6\times6\times6$ large for optimizations, the residual forces on fractional coordinates were less than $4\times10^{-4}$ Ry/au, residual pressure on the unit cell less than 1 kbar. The application of these pseudopotentials has been validated on known properties (structure and workfunction) of crystalline Cs$_2$Te and Cs$_2$Te$_5$. This method provides $a=9.719$, $b=12.178$ and $c=10.407$ Å for the calculated lattice parameters of Cs$_2$Te$_5$, while the experimental ones$^{[13]}$ are $a=9.373$, $b=12.288$ and $c=10.140$ Å, an agreement within 3.5%. There are two different Te-Te bond lengths in Cs$_2$Te$_5$: the calculated values are 2.845 and 3.090 Å, the experimental ones are 2.765 and 3.049 Å, respectively, an agreement within 3%. Experimental and calculated lattice angles are all 90°. Optical absorption spectra have
been calculated in the Random Phase Approximation (RPA) as implemented in the YAMBO code, the spectra were calculated using a gradually increased number of planewaves and interaction block-size until convergence at 20000 plane waves and an interaction block size of 403. For comparison, data for Cs₂Te and Cs₂TeC₂ have been taken from Ref. [5]. The workfunction calculations were based on slabs of at least 30 Å width separated by vacuum layers up to 30 Å following the methodology of Ref. [14]. Only the top and bottom two layers were relaxed while middle layers were kept at the bulk optimum structures.

The two most important crystal surfaces of Cs₂Te₅ that do not cleave the polytelluride anions and have Miller indices of (010) and (110) have been considered. The cleavage of polytelluride anions is energetically unfavorable and would lead to a plethora of possible surface reconstructions. To estimate the strength of the simplest such cleavage, properties of the (001) surface have also been calculated. For the (010) surfaces, two different cleavages have been modeled, (010)-C₁ and (010)-C₂. The (110) and (010)-C₁ surface slabs have identical top and bottom surfaces, while the (010)-C₂ surfaces are not identical. 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.

III. RESULTS AND DISCUSSION

The bandstructure of Cs₂Te₅ is shown in Fig. 3. It indicates a band gap of 0.19 eV, i.e. a small bandgap semiconductor material. The optical absorption spectra of Cs₂Te₅ with different light polarizations are presented in Fig. 4 and are compared to those of Cs₂Te and Cs₂TeC₂. The small gap value and the strong absorption at low photon energies appears to be consistent with the experimentally observed “metallic grey” color of Cs₂Te₅. The workfunction values for several important crystallographic surfaces of Cs₂Te₅ are listed in Table I. It is apparent that the lowest workfunction belongs to the Cs₂Te₅(010)-C₂ surface with fully Cs-covered polytelluride ribbons. The other surfaces have much greater...
RESULTS AND DISCUSSION

FIG. 3: Band structure of Cs$_2$Te$_5$. Energy levels are relative to the top of the valence band. The band gap is 0.19 eV. The selection of the special k-points is based on the orthorombic symmetry of the cell and is identical with that used for Cs$_2$Te in Ref. 5 as both Cs$_2$Te ( space group: Pnma) and Cs$_2$Te$_5$ (space group: Cmcm) crystallize in the orthorombic system.

FIG. 4: Optical absorption spectra in terms of the macroscopic dielectric constant $\varepsilon_M(\omega)$ for Cs$_2$Te$_5$ as compared to that of Cs$_2$Te and Cs$_2$TeC$_2$. The energy of the incident photons is denoted by $\omega$, while the polarization of the photons is indicated by the coordinate directions in the curve-keys with $z$ being parallel with the main crystallographic axis. The calculations predict that Cs$_2$Te$_5$ would have a significantly higher absorption probability at lower photon energies, also at $\approx 1.9$ eV which is the workfunction value of the Cs-covered Cs$_2$Te$_5$ (010) surface.

TABLE I: Calculated properties of Cs$_2$Te$_5$ surfaces: workfunctions ($\Phi$), bandgaps at the $\Gamma$-point $E_g(\Gamma)$ and surface energies ($\sigma$). For the Cs$_2$Te$_5$(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$_2$Te$_5$(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$_2$Te$_5$(010)-C2 slab was 22.6 meV/Å$^2$, the contribution of the Cs-rich side is estimated to be close to the Cs$_2$Te$_5$(010)-C1 value ($\sigma = 7.1$ meV/Å$^2$).

| surface       | $\Phi$ (eV) | $E_g(\Gamma)$ (eV) | $\sigma$ (meV/Å$^2$) |
|---------------|-------------|--------------------|----------------------|
| Cs$_2$Te$_5$(110) | 3.22        | 0.3577             | 7.2                  |
| Cs$_2$Te$_5$(010)-C1 | 3.47        | 0.3344             | 7.1                  |
| Cs$_2$Te$_5$(010)-C2 | 1.87/1.97   | 0.0309             | -                    |
| Cs$_2$Te$_5$(001) | 4.70        | 0.0369             | 20.4                 |

workfunctions, in the 3.2-3.5 eV range or even above for the Cs$_2$Te$_5$(001) cleavage. Also note that cleaving the polytelluride ribbons results in a relatively large surface energy, i.e. it is energetically very unfavorable as compared to the other cleavages.

Comparing the workfunction value of $\approx 1.90$ eV for the Cs-rich one of the Cs$_2$Te$_5$(010)-C2 surfaces to the optical absorption spectra in Fig. 4 one can see a very strong absorption at 1.9 eV. This means that if this surface can be realized, it will have not only a significantly (by more than 1 eV) reduced workfunction, but also an even higher optical absorption than Cs$_2$Te, and as a consequence its quantum yield may be higher than that of Cs$_2$Te. At the same time, Cs$_2$Te$_5$ is just a two-component material and its synthesis is readily available from the literature. It is however also to be noted that the surface energy differences between the (010) and (110) surfaces are very small, making it difficult to realize the Cs-covered Cs$_2$Te$_5$(010)-C2 cleavage without coexisting presence of other sur-
faces. Since large single crystals can be grown of Cs\textsubscript{2}Te\textsubscript{5} as reported in Ref. \cite{10}, the suitable cleavage of them could deliver the required surface. Since the Cs\textsubscript{2}Te\textsubscript{5} material is relatively soft due to the weak interaction between Te-ribbons and the small cleavage energy between Cs-covered Te-ribbons, it may also be deposited along these easy-to-cleave surfaces by rubbing larger crystals of Cs\textsubscript{2}Te\textsubscript{5} to the substrate surface, similarly to deposition of graphite.

Bandgaps of the surface slabs at the Γ-point differ somewhat from the bulk-value (0.19 eV) in the range of \(\approx 0.037-0.360\) eV, being smallest for the lowest workfunction Cs\textsubscript{2}Te\textsubscript{5}(010)-C2 slab.

While the acetylated Cs\textsubscript{2}Te, i.e. Cs\textsubscript{2}TeC\textsubscript{2}, shows very anisotropic workfunction values, surface energies and optical absorptions (a factor of 9 optical absorption differences\cite{5}), the degree of anisotropy is somewhat smaller for Cs\textsubscript{2}Te\textsubscript{5}, where optical absorptions may differ by a factor of two in the visible spectral range.

IV. CONCLUSIONS

In the present study we have computationally analyzed bulk and surface properties of Cs\textsubscript{2}Te\textsubscript{5}, an existing\cite{10} crystalline phase of the Cs-Te system, in order to search for alternatives of Cs\textsubscript{2}Te in the Cs-Te system with reduced workfunctions and high quantum efficiency. We have found that the fully Cs-covered Cs\textsubscript{2}Te\textsubscript{5}(010)-C2 surface has a workfunction of \(\approx 1.9\) eV and a quantum efficiency that is higher than that of Cs\textsubscript{2}Te, both at the respective workfunction values. Since large single crystals of Cs\textsubscript{2}Te\textsubscript{5} can be produced as described in Ref. \cite{10} this prediction can be validated experimentally, and Cs\textsubscript{2}Te\textsubscript{5} can become a practical alternative to Cs\textsubscript{2}Te for photophysical applications.

V. ACKNOWLEDGEMENTS

The authors gratefully acknowledge A. Zholents, Z. Yusof and K. Attenkofer (APS/Argonne) for helpful discussions and thank NERSC (U.S. DOE DE-AC02-05CH11231) for the use of computational resources. This research was supported by the U.S. DOE Office of Science, under contract No. DE-AC02-06CH11357, and also by the National Science Foundation (No. PHY-0969989).

* Nemeth@ANL.Gov

1. E. Taft and L. Apker, J. Opt. Soc. Am. 43, 81 (1953).
2. D. Velazquez, E. E. Wisniewski, Z. Yusof, K. Harkay, L. Spentzouris, and J. Terry, AIP Conf. Proc. 1507, 780 (2012).
3. D. H. Dowell et al., Nuclear Instruments and Methods in Physics Research A 622, 685 (2010).
4. K. Németh et al., Phys. Rev. Lett. 104, 046801 (2010).
5. J. Z. Terdik, K. Németh, K. C. Harkay, J. Jeffrey H. Terry, L. Spentzouris, D. Velizquez, R. Rosenberg, and G. Srajer, Phys. Rev. B 86, 035142 (2012).
6. U. Ruschewitz, Z. Anorg. Allg. Chem. 632, 705 (2006).
7. U. Ruschewitz, Z. Anorg. Allg. Chem. 627, 1231 (2001).
8. H. Billetter et al., Z. Anorg. Allg. Chem. 636, 1834 (2010).
9. D. M. Smith and J. A. Ibers, Coordination Chemistry Reviews 200-202, 187 (2000).
10. P. Boettcher and U. Kretschmann, Z. Anorg. Allg. Chem. 491, 39 (1982).
11. P. Gianozzi et al., J. Phys.: Condens. Matter 21, 395502 (2009), http://www.quantum-espresso.org.
12. J. P. Perdew et al., Phys. Rev. Lett. 77, 3865 (1996).
13. A. Marini et al., Comp. Phys. Comm. 180, 1392 (2009), http://www.yambo-code.org.
14. C. J. Fall et al., J. Phys.: Cond. Mat. 11, 2689 (1999).
FIG. 5: Panels (A) and (B) show the (bc) and (ba) plane views of a 3x3x3 supercell of the Cs₂Te₅ 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.