

Ab initio modelling of Cs₂Te photocathodes

Ab initio modelling of the electronic structure of Cs₂Te for photocathode applications

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In Short

- Understand defect formation (vacancies and substitutional atoms) and their effect on the electronic structure of Cs₂Te
- Clarify which surfaces are likely to form in Cs₂Te based on their energetic stability through high-throughput sampling
- Determine the impact of surfaces on the electronic structure of Cs₂Te

The development of photocathode electron injectors is a relevant technology for free electron lasers and for the new generation of light sources. In light of these technological advances, it is mandatory to achieve full control over the microscopic properties of the materials adopted as photocathodes. Semiconductors like caesium telluride have emerged due to their enhanced quantum yield and relatively low intrinsic emittance [1,2]. These characteristics, which are crucial for the operational performance of the photocathodes, are tightly connected with the structural and electronic properties of the materials. The limitations posed by the surface sensitivity of the systems, their lifetime before degradation, and the overall difficulty in controlling their composition during growth, hinder an in-depth experimental characterization of their intrinsic characteristics. For this reason, *ab initio* methods based on density-functional theory (DFT) are ideally suited to complement experiments to achieve this challenging task.

The overarching goal of this project, with planned duration of 36 months, is to understand the electronic structure of the photocathode material Cs₂Te using DFT, in order to ultimately rationalize and predict its photoemission properties. The scientific question is embedded in a formal collaboration with DESY Hamburg, where Cs₂Te is the material of choice for the photocathodes of the particle accelerators. Understanding the microscopic mechanisms that determine its electronic structure, and consequently its photoemission properties, in the presence of defects, surfaces, and interfaces, is of paramount importance to maximize the lifetime and the functionality of the photocathodes operating in this big facility.

In its most stable form bulk form, Cs₂Te is represented by an orthorhombic crystal with 12 atoms in

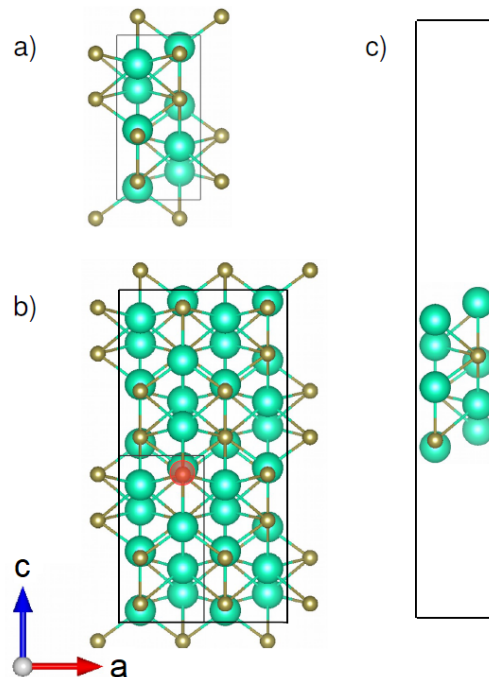


Figure 1: Ball and stick representation of Cs₂Te in a) its unit cell (1x1x1), b) a 2x2x2 supercell, and c) a surface slab non-periodic in one direction. The boundaries of the simulation cell are indicated by black boxes. The red dot indicates a vacancy or a substitutional defect. Cs atoms are depicted in green and Te atoms in gold.

the unit cell, as depicted in Fig. 1a). In order to simulate a realistic defected structure, it is necessary to construct a supercell with a sufficient amount of replicas of the unit cell to feature a reasonable concentration of defects. In Fig. 1b) a (2x2x2) supercell of Cs₂Te is shown, where the red dot marks the position of a defect, which is intended to be either a vacancy or substitutional Cs or Te atom. Such a system includes approximately 1% defect concentration, given by 1 defect every 96 atoms. In Fig. 1c) a slab is sketched of Cs₂Te. In this case it is crucial to construct a supercell that is non-periodic in one direction. This direction is therefore sampled only by one **k**-point and a sufficient amount of vacuum to prevent spurious interactions between neighboring replicas has to be included. The sketch shown in Fig. 1c) represents a slab formed by one unit cell in the non-periodic direction, corresponding to a thickness of approximately 1 nm. Slab thicknesses of approximately 12 nm ensure a realistic description of the surface properties.

In preparation for this project, we investigated the electronic structure of bulk Cs₂Te. The density of states (DOS), with atomic contributions projected for

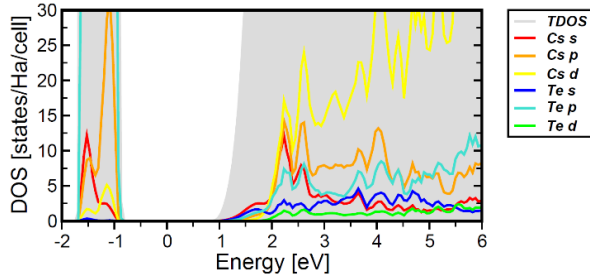


Figure 2: Density of states (DOS) of Cs_2Te computed from DFT. The total contribution is depicted by the shaded grey area while atom-projected contributions are displayed in color according to the legend.

each atomic species, is depicted in Fig. 2. The total DOS is also plotted for reference. From this result we notice that Cs_2Te has a gap of approximately 1.80 eV, as obtained from semi-local DFT. The valence region is here represented by a relatively sharp peak with pronounced p -character stemming from both Cs and Te species. On the contrary, the bottom of the conduction band is dominated by s -states Cs and Te, which, due to their spherical symmetry, give rise to parabolic bands. We also notice that at higher energies d -states from Cs atoms mostly contribute.

In this project we will investigate the defect stability and their impact on the electronic structure of bulk Cs_2Te . We will focus on Cs and Te vacancies as well as corresponding substitutional defects (*i.e.*, a Cs atom occupying a Te site and vice versa) which most commonly characterize Cs_2Te samples based on the experimental growth conditions. To determine the formation energy of such defects, we will first optimize the defected structures by minimizing the interatomic forces. With the optimized structure we will subsequently determine the defect formation energy as the difference between the total energy of the defected and pristine system. The size of the simulation supercell will be tuned to determine realistic defect concentrations. For example, concentrations of approximately 0.3% are obtained with a $(3 \times 3 \times 3)$ supercell. Defected systems will be automatically generated using a self-written script. In this way, we aim to randomize the position of the defect in the cell and to access a more realistic configuration space. Adopting this approach, we will consider single and double vacancies and/or substitutional defects of the type mentioned above. An automated algorithm to combine the band structures and DOS obtained for all the runs will be developed based on the ideas presented in Ref. 3 for random alloys.

An additional aspect that we will investigate in the first phase of the project is the energetic stability and the electronic structure of specific surfaces. In this analysis, we will consider the 23 surfaces described by all possible combinations of Miller indices 0, 1,

and 2. These structures will be simulated by slabs with 12 nm thickness in the non-periodic direction. The smallest possible unit-cell size in the two periodic directions will be used. A vacuum layer of $\sim 30\text{\AA}$ thickness, as estimated in the preparatory work, will be included to between the replicas. Neglecting thermodynamic effects, the surface energy required to form the surface area A will be computed as

$$E_{surf} = \frac{1}{A}(E_{tot} - N_{Cs}\mu_{Cs} - N_{Te}\mu_{Te}),$$

where E_{tot} is the total energy as obtained from DFT calculations, N_{Cs} and N_{Te} are the number of Cs and Te atoms, respectively, while μ_{Cs} and μ_{Te} their chemical potentials. It is worth noting that, again assuming zero temperature and pressure, the total energy of the bulk is given by $E_{bulk} = N_{Cs}\mu_{Cs} - N_{Te}\mu_{Te}$.

All calculations will be carried out from DFT (PBE exchange-correlation functional 5) with the all-electron full-potential code FHI-aims 4, adopting numerical atom-centered orbitals as basis set. In this framework, an efficient grid-based parallelization scheme is implemented with grid points distributed into localized batches spread across all available CPUs. In periodic systems, the \mathbf{k} -points offer an additional parallelization layer. FHI-aims is very efficient when dealing with supercells containing a large amount of vacuum. Moreover, being an all-electron code, it gives direct access to the energies of the core electrons, thus providing valuable information for comparison with experimental XPS spectra measured by our project partner in DESY Hamburg,

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More Information

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Project Partners

Dr. Sven Lederer, Maschinen Vakuum Systeme, DESY Hamburg

Funding

DESY Hamburg