

TELLURIUM ADSORBED ON TlInTe₂ STRUCTURES FOR ADVANCED ENERGY APPLICATIONS

S.S. HUSEYNOVA, S.O. MAMMADOVA

Institute of Physics Ministry of Science and Education of Azerbaijan,

AZ 1143, Baku, H. Javid Ave., 131

memmedova_seide.fiz@mail.ru

The work presents the results of the modeling of the adsorption of tellurium on the surface of $2 \times 1 \times 1$ TlInTe₂ structure. The research was carried out by computer modeling using the Atomistic Toolkit software. The calculations were performed at different degrees of coverage of the TlInTe₂ surface with adatoms to find out the effect of these structural changes on the energy. The paper includes models of the studied objects, along with tables presenting the adsorption energy and the magnitude of the distance between the adsorbate and the atoms.

Keywords: TlInTe₂ structure, adsorption, density functional theory (DFT).

1. INTRODUCTION

The structural and electronic properties of the TlInTe₂ are investigated experimentally [1] and theoretically [2,3,4]. Upon defect formation of the TlInTe₂, as well as during the substitution of both cations and anions can be changed properties of compound. The structure of TlInTe₂ can be described as composed of two subsystems, namely, the indium subsystem with a negative charge ($\text{In}^{3+}\text{Te}^{2-}_2$), which is arranged in parallel with crystallographic axis *c* and form chains, and the unstable thallium subsystem located between the chains. The weak Tl–Te bond in the thallium sublattice is one of the reasons for its instability, being nearly two times weaker compared to the In–Te bond according to the provided data [5].

The interatomic distances for Tl–Te and In–Te bonds in the structures are 3.6 Å and 2.82 Å, appropriately [6]. Zintl compounds such as InTe [7], TlSe [8], and TlInTe₂ [9] exhibit both covalent (stronger) and ionic (weaker) substructures within them. The presence of such hierarchically bonded sublattices makes Zintl compounds ideal for intrinsically ultra-low thermal conductivity.

The [10] work demonstrates that the stoichiometric excess of the additive atom in the TlInTe₂ crystal with a chain structure allows to purposeful control the anisotropic properties of materials. This method holds potential for application in the development of fast conversion system.

The purpose of this study is the ab initio calculation of the energy of Te adsorption by the surface of TlInTe₂ supercells. Theoretical investigations on the adsorption of tellurium on the TlInTe₂ surface reveal that the calculated adsorption energy characteristics depend on several factors, including the calculation technique, adatom structure, adsorption site (top, bridge, or hollow position), the bond distance (*d*) between the adatom and the surface, and the nature of the interaction between the adatom and the TlInTe₂ structure.

2. ODEL AND CALCULATION PROCEDURE

Firstly, we perform a structural optimization for Te adsorbed on TlInTe₂ supercell within the framework of DFT using Perdew–Zunger (PZ) exchange correlation functional, as implemented in the Atomistic ToolKit. The kinetic cut-off energy is set to 150 Ry. During the structure optimization, the reciprocal space is sampled by a $5 \times 5 \times 5$ k-point mesh. The primitive cell of TlInTe₂ was relaxed and optimized with force and stress tolerances of 0.01 eV/Å and 0.01 eV/Å³, respectively. The geometry, electron band structure and adsorption energy Te adsorbed on TlInTe₂ supercell have been studied theoretically.

3. RESULTS AND DISCUSSION

TlInTe₂ belongs to the TlSe-family and has a simple tetragonal crystal structure with the space group I4/mcm. Fig. (a) presents the atomic structure of $2 \times 1 \times 1$ TlInTe₂ supercell, (b) and (c) corresponds to the bridge and hollow adsorption sites of Te adsorbed on $2 \times 1 \times 1$ TlInTe₂ supercell. Each In^{3+} makes four covalent bonds with its four nearest Te^{2-} ions forming the anionic chains along the tetragonal *c*-axis. Each Tl^+ cation is surrounded by eight Te^{2-} ions, forming skewed cages referred to as Thompson cubes [11,12]. The relaxed lattice parameters are $a = 8.7 \text{ \AA}$ and $b = 7.33 \text{ \AA}$, in agreement with previous calculations and experimental measurements [11,12]. Due to the sp^3 hybridized In, TlInTe₂ adopts a Zintl-like structure and exhibits semiconducting properties.

Adsorption energy can be defined as the decreasing energy while two materials are combined under the adsorption process in which an atom, ion, or molecule (adsorbate) is attached to the surface of a solid (adsorbent). This energy is mainly used when calculating the chemical engineering properties, exploring the adsorption mechanism, or determining the energetic heterogeneity of the surface of a solid [13].

To analyze the Te atom adsorption on the TlInTe₂ surface, we used the following formula for the energy.

$E_{\text{ads}} = E_{\text{total}}[\text{Te}_{\text{ads}} + \text{TlInTe}_2] - E[\text{Te}_{\text{ads}}] - E[\text{TlInTe}_2]$
 $E_{\text{total}}[\text{Te}_{\text{ads}} + \text{TlInTe}_2]$ is the total energy of a TlInTe₂ system adsorbed by a Te atom. $E[\text{TlInTe}_2]$ is the total energy of a TlInTe₂, and $E[\text{Te}_{\text{ads}}]$ is the energy of one atom Te.

The energies $E_{\text{total}}[\text{Te}_{\text{ads}} + \text{TlInTe}_2]$ and $E[\text{TlInTe}_2]$ were obtained from a system with an optimized structure using the DFT method. The adsorption energies are different because the total energies with and without optimization take different values. Thus, whether the adsorption is more stable or not depends on the optimization of the system.

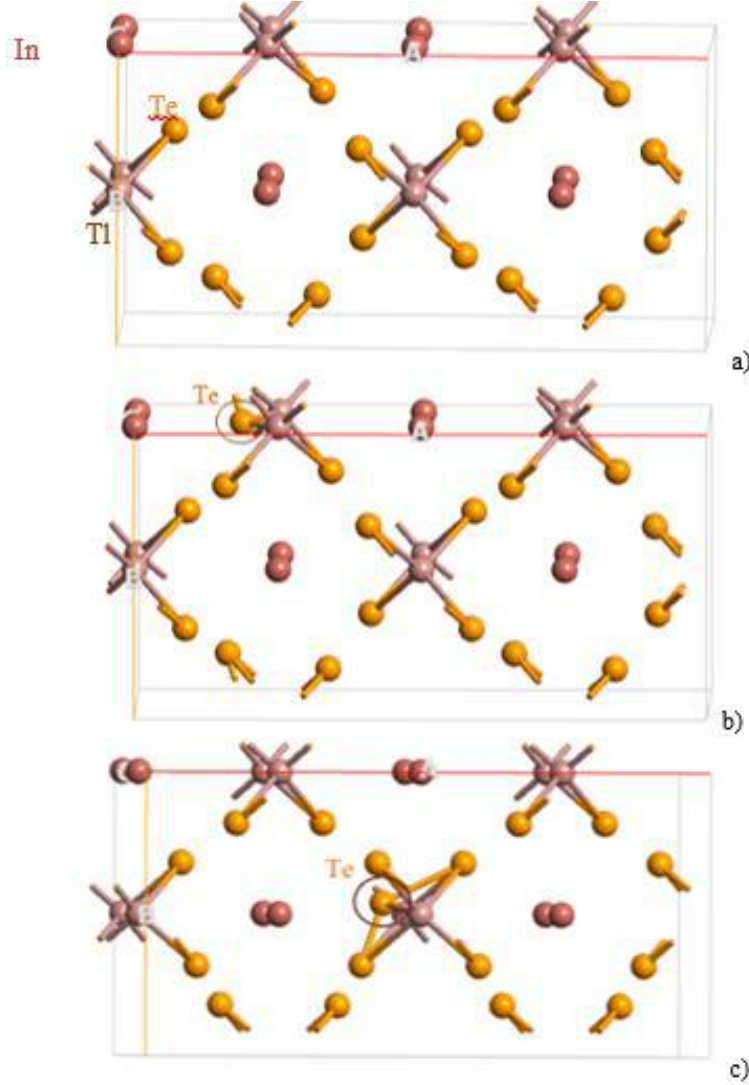


Figure. Atomic structure of 2×1×1 TlInTe₂ supercell (a). The B (b) and H (c) correspond to the bridge and hollow adsorption sites of Te adsorbed on 2×1×1 TlInTe₂ supercell.

Table.

Adsorption energy and bond length						
Te adsorbed on 2×1×1 TlInTe ₂ supercell	Position of the adatom	E_{tot} (eV)	E_{ad} (eV)	$d_{\text{Te-In}}$ (Å)	$d_{\text{Te-Te}}$ (Å)	$d_{\text{Te-Tl}}$ (Å)
with an optimized structure	B	-21393.27271	-53.97494	1.1204	2.8977	2.8721
	H	-21380.21787	-40.9201	2.3091	1.3574	--
without an optimized structure	B	-18998.4731	-64.52765	1.5729	--	--
	H	-18959.47645	-25.531	1.894	2.0283	--

In the bridge adsorption site (B), there is a bond between Te and In before optimization. However, after optimization, a bond forms not only between Te and In but also with Tl and Te atoms. Therefore, in this case, the value of the adsorption energy (Table) with an optimized structure is greater than that without an optimized structure. On the other hand, in the hollow

adsorption site, the situation is reversed. It is known that in the case when the adsorption energy is negative, the system under study is characterized by stability. Thus, in connection with this statement, it follows that all the considered configurations of adsorption of Te adatoms on the surface of the TlInTe₂ supercell are stable at any degree of coverage.

- [1] Al-Ghamdi, A.A., Nagat, A.T., Al-Hazmi, F.S., AlHeniti, S., Bahabri, F.S., Mobarak, M.M., and Alhar-bi, S.R., Growth and electrical characterization of TlInTe₂ single crystal, J. King Abdulaziz Univ. Sci., 2008, vol. 20, pp. 27–38.
- [2] Ding, G., He, J., Cheng, Z.X., Wang, X., and Li, S., Low lattice thermal conductivity and promising thermoelectric figure of merit of zintl type TlInTe₂, J. Mater. Chem. C, 2018, vol. 6, pp. 13269–13274. <https://doi.org/10.1039/c8tc034>
- [3] Jana, M.K., Pal, K., Warankar, A., Mandal, P., Waghmare, U.V., and Biswas, K., Intrinsic rattler-induced low thermal conductivity in zintl type TlInTe₂, J. Am. Chem. Soc., 2017, vol. 139, no. 12, pp. 4350–4353. <https://doi.org/10.1021/jacs.7b01434>
- [4] M. M. Asadov, S. N. Mustafaeva, S. S. Guseinova, and V. F. Lukichev, ISSN 1063-7397, Russian Microelectronics, 2023, Vol. 52, No. 1, pp. 21–31. Pleiades Publishing, Ltd., 2023, Vol. 52, No. 1, pp. 46–57, DOI: 10.1134/S1063739722700196
- [5] N. Kh. Abrikosov, V. F. Bankina, L. V. Poretskaya, E. V. Skudnova, and S. N. Chizhevskaya, Semiconducting Chalcogenides and Alloys on their Basis (Nauka, Moscow, 1975) [in Russian].
- [6] D. Muller, G. Eulenberger, and H. Hahn, “Über ternäre Thalliumchalcogenide mit Thallium selenidstruktur,” Z. Anorg. Allg. Chem. 398, 207 (1973)
- [7] M. K. Jana, K. Pal, U. V. Waghmare, K. Biswas, Angew. Chem. Int. Ed. 2016, 55, 7792–7796.
- [8] M. Dutta, S. Matteppanavar, M. V. D. Prasad, J. Pandey, A. Warankar, P. Mandal, A. Soni, U. V. Waghmare, K. Biswas, J. Am. Chem. Soc. 2019, 141, 20293–20299.
- [9] a) M. K. Jana, K. Pal, A. Warankar, P. Mandal, U. V. Waghmare, K. Biswas, J. Am. Chem. Soc. 2017, 139, 4350–4353; b) G. Ding, J. He, Z. Cheng, X. Wang, S. Li, J. Mater. Chem. C 2018, 6, 13269–13274; c) M. Wu, Enamullah, L. Huang, Phys. Rev. B 2019, 100, 075207.
- [10] R.S. Madatov, K.H. Xalilova, A.I. Najafov, M.A. Mammadov, G.M. Isgenderova, M.M. Shirinov, Effect of electric field and temperature on conduction anisotropy in TlInTe₂-Te crystals, Transactions of Azerbaijan National Academy of Sciences Physics and Astronomy, v. XLI, № 2, Baku-2021, p. 65–72.
- [11] M. K. Jana, K. Pal, A. Warankar, P. Mandal, U. V. Waghmare and K. Biswas, J. Am. Chem. Soc., 2017, 139, 4350–4353.
- [12] K. Wakita, Y. Shim, G. Orudzhev, N. Mamedov and F. Hashimzade, Phys. Status Solidi A, 2006, 203, 2841–2844.
- [13] Rouquerol, J., Rouquerol, F., Llewellyn, P., Maurin, G. and Sing, K.S.W. (2013) Adsorption by Powders and Porous Solids: Principle, Methodology and Applications. 2nd Edition, Academic Press, New York.