

NATURE OF INTERLAYER BONDS IN TWO-DIMENSIONAL DITELURIDES

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In our work, by using first-principles calculations we perform a systematic study of the interlayer bonds and charge redistribution of ditelurides (NiTe₂, PdTe₂, PtTe₂). Our results demonstrate, that bonds in ditelurides can be associated with so-called dative chemical bonds between layers.

So-called van der Waals heterostructures constructed from various monolayer are also considered as key materials with multiple prospective applications almost in all areas. Results obtained in experimental studies [1] demonstrate a significant influence of the number and quality of subsurface layers on chemical activity of surface of few-layer graphene systems and other 2D materials. Therefore, significance of bonds between the neighbouring layers is essential for understanding of physical and chemical properties of these structures and further intelligent design of novel layered material.

The simulations of atomic and electronic structure of all considered materials were carried out within Density Functional Theory (DFT) framework implemented in the Vienna ab-initio simulation package (VASP) [2]. We also included van der Waals interaction using the method of Grimme (DFT-D3) [3]. These first-principles results were used for estimation of the binding energy:

$$E_b = E_m - E_b/n$$

where E_m and E_b are the total energies of monolayer and bulk supercells, correspondingly. n denotes the number of layers in the unit cell used to simulate the bulk phase. To quantitatively estimate the charge redistribution corresponding to formation of the bulk structure from the individual monolayers we have calculated the charge density difference defined as:

$$\Delta\rho = \rho_b - \sum_i^n(\rho_i)$$

Here ρ_b corresponds to the electron density of the supercell having periodic boundary conditions, containing several layers and representing the bulk crystal. In turn, ρ_i is the electron density of the i -th monolayer isolated from the rest of the supercell.

Results of our simulations demonstrate that ditelurides (NiTe₂, PtTe₂, PdTe₂) characterized by comparably long distance of the ionic radii of cations, which makes possible additional coordination of metal centers by orbitals of cations belonging to other layer. What is being implemented by values of E_b are larger than 600 meV and

close to those estimated for the bonds in systems with coordination (also called dative) bonds [4] between metal centres and ligands or molecule. As the result so-called dative or coordination chemical bonds between neighbouring layers are formed in ditelurides. Such a coordination types of the interlayer bonds leads to visible changes in electronic structure of ditelurides within monolayer/bulk transition. Interlayer bonds are responsible for amplifying three-dimensional character of inter-atomic couplings in these systems. The same coordination-like inter-layer interactions also contribute to the formation of unsaturated chemical bonds on the surface, which explains experimentally observed chemical instability of ditelurides. Redistribution of the charge density upon formation of coordination interlayer bonds can be the key to understanding of charge density waves observed in multiple dichalcogenides.

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