DFT study of the interplay between structural and electronic properties of $CuInP_2S_6$/$CuInP_2Se_6$ heterostructures

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ABSTRACT

Contemporary material science is in continuous searching for new materials with extraordinary or better-then-previous properties. In this connection, heterostructures based on complex but already known compounds are almost an endless source of new perspective functional materials. Layered ferroics of $CuInP_2S(Se)_6$ type are ones of such nontrivial semiconducting crystals, which even by their own possess a wide variety of interesting properties, especially those of them, connected with metal sublattices instability making them intriguing for both fundamental science and applications [1-3].

Density functional theory was utilized for the simulation of energy states of electronic subsystems of $CuInP_2Se_6$/$CuInP_2S_6$ heterostructures with different layers' thicknesses. Also, the structural relaxation for the considered set of layered heterostructures was conducted. The dependencies of In and Cu atoms' sublattices ordering on the composition of layers and their number have been observed.

STRUCTURE PARAMETERS

The $(CuInP_2Se_6)_m$/$(CuInP_2S_6)_n$ heterostructures with different m/n (1/1, 1/3, 2/2, 3/1) ratio, were used for simulation of energy structure.

Initial materials ($CuInP_2Se_6$ (CIPSe) and $CuInP_2S_6$ (CIPS)) has the following lattice parameters;

CIPSe:
$a_1 = a_2 = 6.40$ Å, $a_3 = 13.36$ Å (hex. latt.)
and CIPS:
$a_1 = a_2 = 6.06$ Å, $a_3 = 13.70$ Å (monocl. latt.)

The DFT with LDA-D approximation was used for preliminary structure relaxation of depicted heterostructures. The next tendencies have been observed:

1) Cu ions in CIPSe layers tend to the middle of corresponding layer's packages;
2) PSe_3 triangles rotate around P-P bonds direction, while CIPS layers shift remaining in their orientation;
3) Both types of above-mentioned transformations amplitudes increase on CIPSe layers number n.
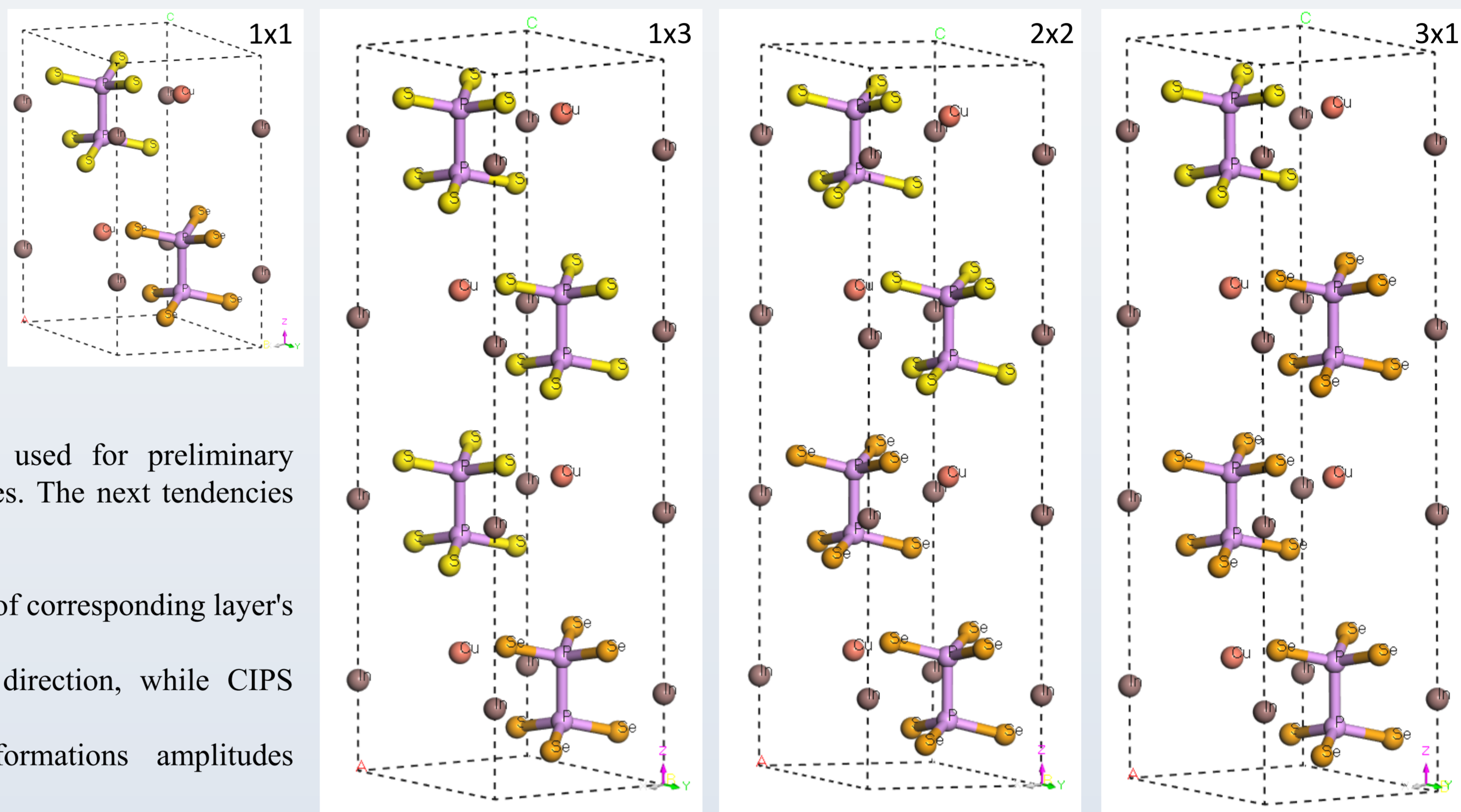
CALCULATED ENERGY PARAMETERS
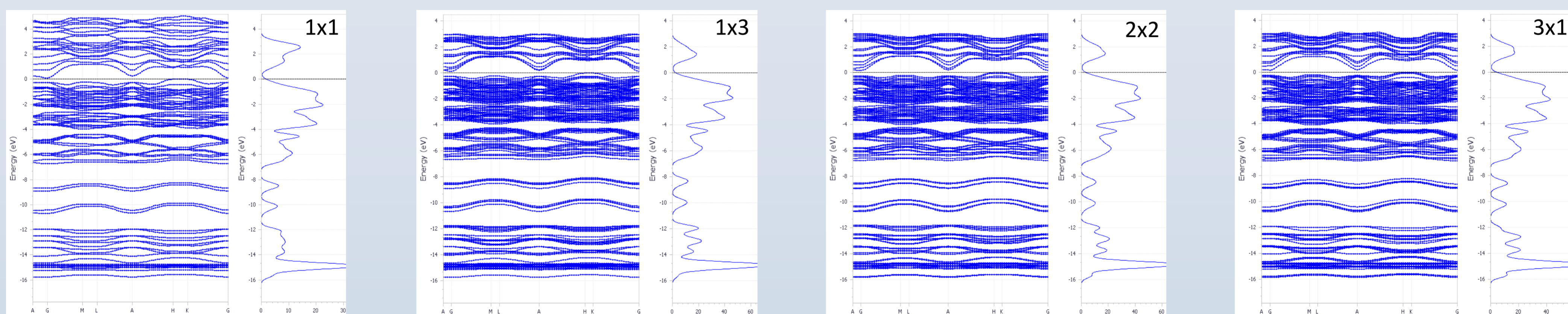
m, layers	n, layers	Etot, Ha	Ebind/Nat, eV	Eg, eV
1	-	-6408.516	-3.854	0.491
-	1	-6775.613	-4.298	1.599
1	1	-6592.004	-3.993	0.102
1	3	-13367.493	-4.061	0.143
2	2	-13184.007	-3.992	0.164
3	1	-13000.520	-3.923	0.157

The energy band spectra, total energies, binding energies, and energy gaps for considered heterostructures are showed in this section. Also the same energy parameters for pure CIPSe and CIPS are included in the Table.

Binding energy deviations are small in comparison to energy gap decreasing. This can be explained by more dense redistribution of valence density between layers in heterostructures, and increasing of the local dipoles' screening.

Conclusions. Following our simulation's findings, the energy gap (and the total ionicity of the chemical bonding) essentially decrease on forming heterostructures on the basis of CIPS and CIPSe in comparison to initial pure materials. The polarity of Se-containing layers also decreasing due to Cu ions shift from quasi-trigonal layer-edge positions towards the middle of the layers' distorted octahedral sites. The shift of CIPS layers is mostly planar and allows to expect increasing in-plane components of polarization, controlled by heterostructure composition. Described transformations of energy properties approve considered heterostructures as perspective materials for functional electronic devices development.

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2. *Zhao M., Gou G., Ding X., and Sun J.* An ultrathin two-dimensional vertical ferroelectric tunneling junction based on $CuInP_2S_6$ monolayer // Nanoscale.-2020.-**12**.-P. 12522-12530.
3. *Huang W., Wang F., Yin L., et al.* Gate-Coupling-Enabled Robust Hysteresis for Nonvolatile Memory and Programmable Rectifier in Van der Waals Ferroelectric Heterojunctions // Adv. Mater.-2020.-**32**.-P. 1908040(9).