

Peculiarities of the Elementary Energy Bands Formation and the Spatial Electron Density Distribution in Crystals of the In-Se System

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After the discovery of excellent thermoelectric properties of the single crystalline rhombic semiconductor In_4Se_3 that are quantified by the dimensionless figure of merit, ZT , that appeared to be larger than 1.4 [1], an intensive research of the indium selenide group has re-started. The phase diagram of the In-Se system shows the existence of InSe , In_2Se_3 , In_4Se_3 , and In_6Se_7 layered crystals. With the increase of the indium content in the compounds of the system, the decrease in their symmetry is observed, together with more complex chemical bonding in these compounds.

In this work the investigation of the *ab initio* band structure and the spatial electron density distribution of the In-Se system in the framework of the DFT and the elementary energy bands concept [2] is presented. It gives us the reliable information about the valence band structure and the peculiarities of the chemical bonding in these crystals. The regularities in the evolution of the elementary energy bands topology is established, together with the choice of the actual Wyckoff position that is responsible for this topology and, at the same time, for the valence band formation in the InSe , In_2Se_3 , In_4Se_3 , and In_6Se_7 crystals. The calculation results show that the localization of a considerable valence electron density between the respective pairs of atoms takes place in all crystals of the system. This indicates the dominance of the covalent type of bonding in the considered compounds. The calculated Mulliken's charges and the degree of ionicity allow to estimate the character of chemical bonding in these crystals. The largest degree of ionicity is obtained for the In_2Se_3 crystal which, in comparison with other indium selenides, has the largest forbidden energy gap.

In the case of $\beta\text{-InSe}$ and In_4Se_3 crystals, the inverse anisotropy of their chemical bonding in the real space is the main factor leading to the anomalous behavior of the dispersion law of charge carriers, which manifests itself as a low-energy nonparabolicity of the valence and conduction band extrema [3]. This peculiar shape of the dispersion law of charge carriers in In_4Se_3 is crucial for the creation of the localized electron condensation states that seem to be responsible for the enhanced thermoelectric properties of this semiconductor [4,5]. Our calculation results show that similar peculiarities of the dispersion laws occur in the band spectra of two further layered polytypes of InSe crystal, the $\epsilon\text{-InSe}$ and $\gamma\text{-InSe}$ ones, which are related to the anomalous character of interlayer interaction present in these compounds.

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