Band gap variation of 2D CdTe slabs in the sphalerite phase and in the phase with boundary chalcogen atoms

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Reducing the thickness of semiconductors to the limit of a few monolayers often leads to emergence of new properties. In this work, the thickness dependence of the band gap of cadmium telluride slabs in both the sphalerite phase and in the inverted phase is studied using the density functional theory method. The sphalerite phase is characterized by Cd−Te−Cd−Te alternating atomic planes, while in the inverted phase the order of planes is Te−Cd−Cd−Te. It is shown that using slabs with a thickness of one to several monolayers variable-gap structures can be fabricated.

Keywords: cadmium telluride, 2D materials, bandgap variation, monolayer.

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After the discovery of the unique electronic properties of graphene, interest in the search for new 2D materials, especially with semiconductor properties, increased, which led to intensive studies of transition metal dichalcogenides [1,2], semiconductors $A^{III}B^{VI}$ [3], as well as topological insulators such as Sb_2Te_3 and Bi_2Te_3 [4]. In all these materials, the covalently bonded layers are held together by weak van der Waals (vdW) forces, which explains their alternative name „vdW" crystals. Of particular interest is the fact that in most of these materials the vdW gap is formed between atomic planes of heavy chalcogen atoms (Se, Te). Reducing the thickness of semiconductors to several monolayers often leads to structural relaxation and the appearance of new properties [5–8]. This served as an incentive to study the electronic structure of 2D cadmium telluride (CdTe) both in the sphalerite (zinc blende) phase with a thickness of 1−4 monolayer (ML), and in the phase formed by inverted blocks inv-2ML (1 vdW = inv-2ML) 1−3 block thick. The sphalerite phase is characterized by alternating layers of Cd−Te−Cd−Te (Figure 1, *a*) while a vdW crystal consists of 1 vdW blocks with a thickness of two monolayers, the outer planes of which are formed by chalcogen atoms, and the metal atoms are located inside the block (Figure 1, *b*). Since there may be an energy barrier between the structure of the slab in the sphalerite phase and the inverted structure of the inv-2ML slab, preventing the structural relaxation of the sphalerite phase, the inverted structure was constructed manually by mutually rearranging the Cd and Te atoms in the upper monolayer. By monolayer ML we mean a relief layer of Cd−Te (see Figure 1). Previously, both slabs 2ML and inv-2ML were completely relaxed by the density functional theory (DFT) [5] method. It turned out that inv-2ML is energetically more favorable than 2ML (the gain in energy per formula unit was 271 meV).

In this work, for the previously obtained relaxed structures, we calculated energy bands, densities of states (DOS) and partial densities of states (PDOS) using the plane-wave code CASTEP [9,10] by the DFT method in the generalized gradient approximation (GGA) with the exchange-correlation functional in the form PBE [11] and vdW corrections Grimme-D2 [12], both without taking into account the spin-orbit coupling (SOC) and with it taken into account. To describe the interaction of valence electrons with the core, scalar-relativistic pseudopotentials were used in calculations without taking SOC into account and fully relativistic (*J*-dependent) pseudopotentials were used in calculations taking SOC into account.

Figure 1 shows the band structures of the 2ML CdTe slab in the sphalerite phase (Figure 1, *a*) and the inv-2ML slab (Figure 1, *b*) calculated by the DFT method. The band gap for the 2ML slab turned out to be close to zero, while the inv-2ML slab is a direct-gap semiconductor at the Γ-point with a minimum band gap ~ 1 eV.

Figure 2 shows graphs of changes in the band gap for slabs and bulk crystals of both phases, both taking into account SOC (red line) and without taking SOC into account (blue dotted line). Meanwhile, it should be borne in mind that the values of the band gaps shown in the graphs are underestimated by 50−60%, which is inherent in the DFT method in the GGA approximation for the exchange-correlation functional due to the incomplete exclusion of electron self-interaction [13,14]. From Figure 2, *a* it is clear that the band gap changes little during the transition from bulk CdTe in the sphalerite

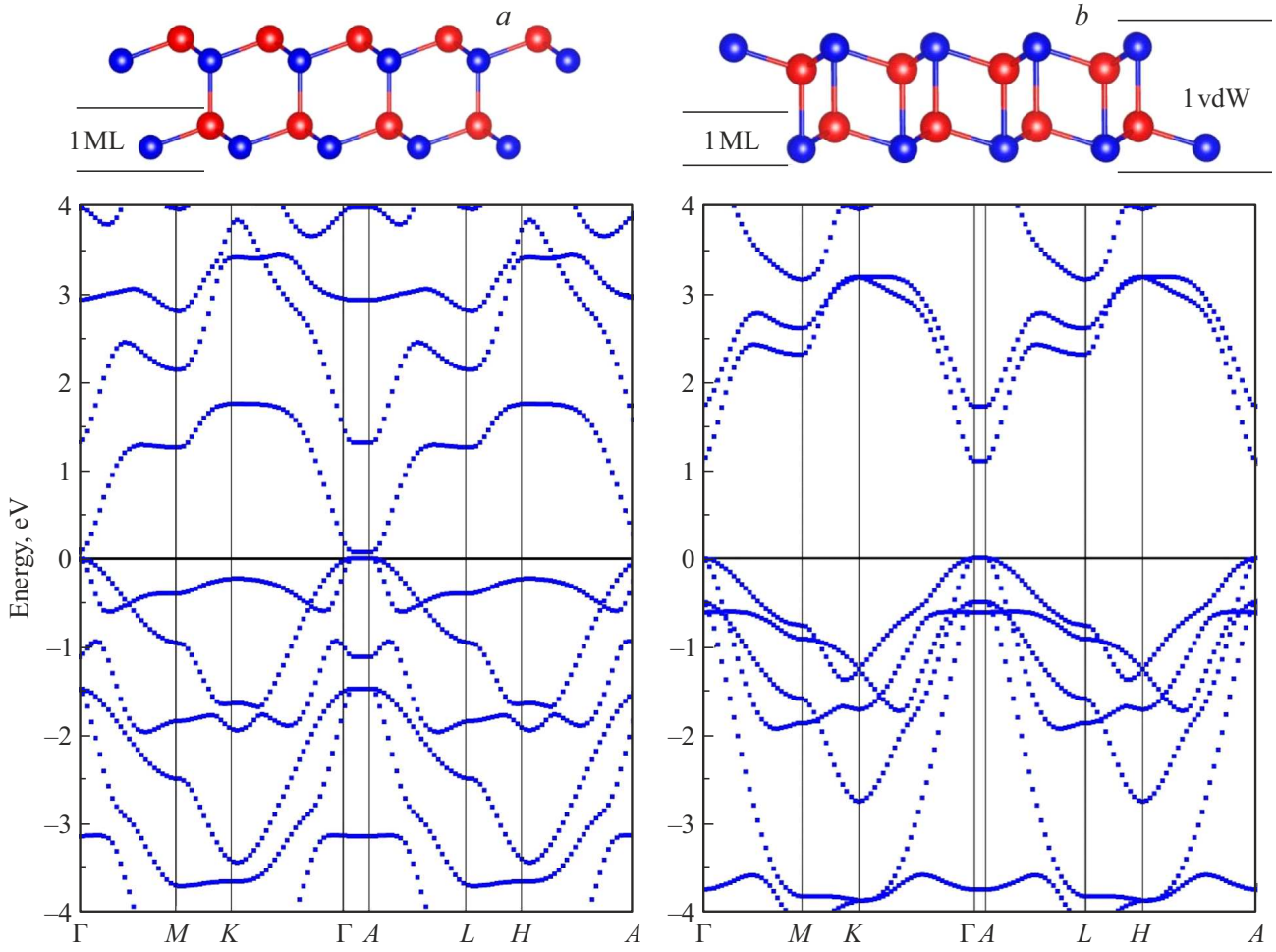

Figure 1. Band structure CdTe in the sphalerite phase with a thickness of 2ML (*a*) and in the inverted phase with a thickness of 1 vdW block (inv-2ML) (*b*). The structures 2ML and inv-2ML are presented at the top of the figure. Cd — red, Te — blue. (A color version of the figure is provided in the online version of the paper).

phase to a 2ML slab and has a value close to zero. With a further decrease in the slab thickness to one monolayer, there is a sharp increase in the band gap value to 1.2 eV. It is also clear from Figure 2, *a* that taking into account SOC leads to a significant increase in the band gap only in the case of bulk material. For slabs with a thickness of 1–4 monolayers, taking into account SOC does not lead to a significant change in the band gap. Figure 2, *b* shows the nature of its change for CdTe in the inverted phase. It can be seen that when going from a slab with a thickness of 1 vdW block to a slab with a thickness of 3 vdW block and then to a bulk vdW crystal, the band gap decreases. Thus, based on the calculations performed, it can be concluded that for the fabrication of variable-gap structures, it will be optimal to use slabs with a thickness of one to several monolayers of CdTe in the sphalerite phase and one or several vdW blocks in the inverted CdTe phase.

Comparison of the theoretical dependence of the band gap of CdTe slabs on their thickness obtained in this work with published experimental data [7,8] showed the consistency of theoretical and experimental results.

The calculated PDOS allowed to determine that the top of the valence band of CdTe both for bulk material and for slabs with a thickness of 1–4 monolayer is formed from *p*-states of tellurium, and for thin slabs there are clearly defined peaks, the number of which equal to the number of monolayers. The bottom of the conduction band includes equally the *p*- and *s*-states of Cd, as well as the *s*-states of Te, with the latter located higher in energy.

In the inverted phase of CdTe, the material is direct-gap for all slab thicknesses, and the band gap decreases as the number of vdW blocks increases: from 1.1 eV for a slab with a thickness of 1 vdW block up to 0.6 eV for both a slab with a thickness of 3 vdW block, and for a bulk vdW crystal (see Figure 2, *b*). Taking into account SOC leads to a decrease in the band gap by 0.1 eV for slabs of thickness 1 and 2 vdW block, and to its slight increase by several hundredths eV for a slab of 3 vdW blocks and bulk vdW crystal.

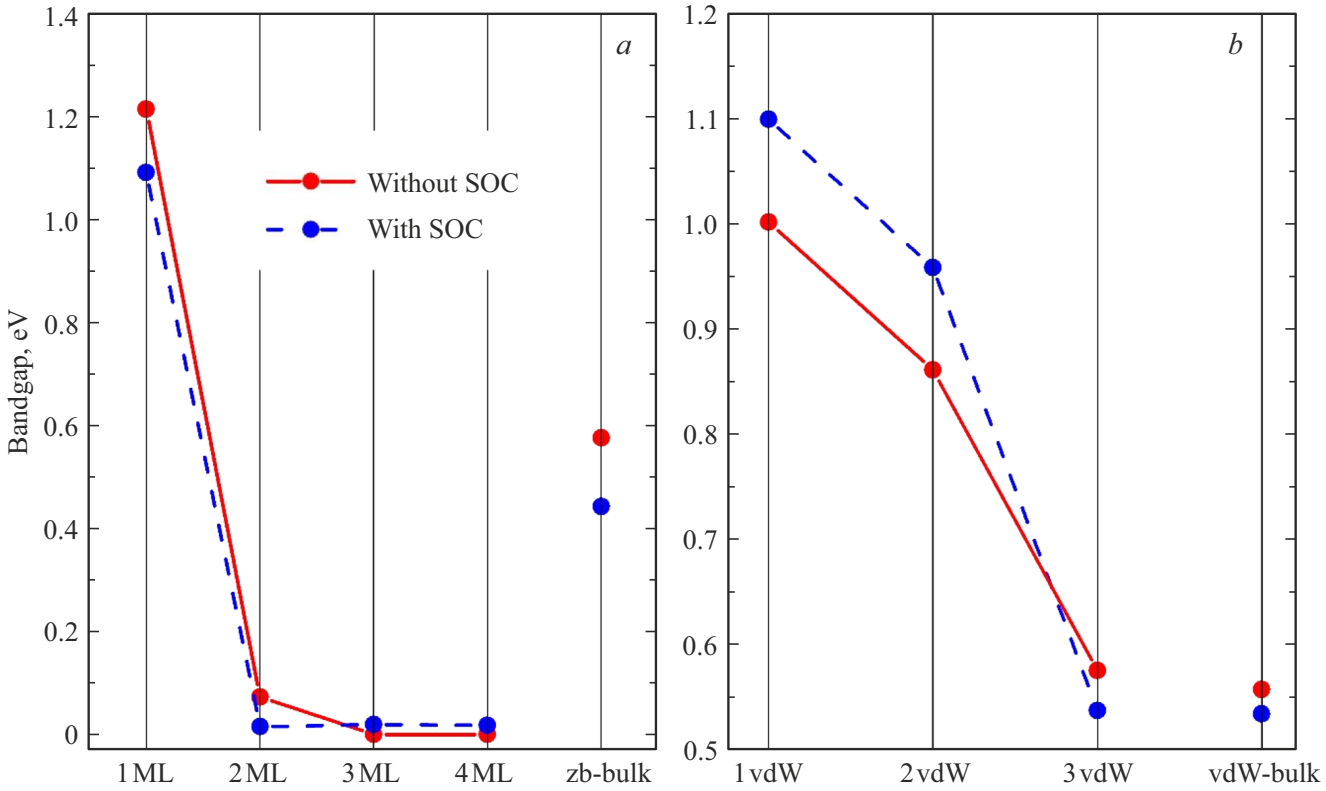

Figure 2. Change in the band gap depending on the number of layers CdTe in the sphalerite phase (*a*) and in the inverted phase (*b*). Red straight line — taking into account spin-orbit interaction, blue dotted line — without taking into account spin-orbit interaction. (A color version of the figure is provided in the online version of the paper).

From PDOS calculations of the inverted phase CdTe it follows that, as in the case of the sphalerite phase with a thickness of 1–4 monolayer, the top of the valence band is formed from *p*-states of Te, and the bottom of the conduction band equally includes *p*- and *s*-states of Cd. It is interesting to note that in the case of a vdW crystal, the number of peaks PDOS of *p*-states of Te in the valence band is one more in the case of extremely thin slabs with a thickness of 1 vdW block, which may be associated with the number of external atomic planes, formed by chalcogen atoms.

Thus, in the work, using the DFT method in the generalized gradient approximation with the exchange-correlation functional PBE and taking into account the van der Waals corrections D2, calculations of band structures and electronic densities of states, both full and partial, were carried out for CdTe in the sphalerite phase for slabs with a thickness of 1–4 monolayer and for CdTe in the inverted phase for slabs with a thickness of 1–3 vdW block. The nature of the change in the band gap of these materials with changes in the thickness of the slabs has been studied. The calculations carried out allowed us to conclude that to obtain variable-gap structures, it is optimal to use thicknesses from one to several monolayers for CdTe in the sphalerite phase and from one to several vdW blocks for CdTe in the inverted phase.

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Conflict of interest

The authors declare that they have no conflict of interest.

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