Ab initio studying of topological insulator Bi$_2$Se$_3$
under the stress

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Abstract. A topological insulator is an unusual state of quantum matter which, while being an insulator in the bulk, has topologically protected electronic states at the surface. These states could be used in different applications, such as spintronics and quantum computing. However, it is difficult to distinguish the surface and bulk contributions into transport properties, such as conductivity. In order to distinguish surface and bulk contributions an external pressure could be applied. In the present work we have performed ab initio calculations of topological insulator Bi$_2$Se$_3$ under the stress for bulk and surface models. Calculations have been made by means of density functional theory within generalized gradient approximation, the spin-orbit interaction was taken into account as well.

It was found that topologically protected surface states remains robust under the stress. Moreover, pressure tends to increase the Fermi velocity of surface electrons, as well as increase electronic density of states at the bottom of the conduction band of the bulk of Bi$_2$Se$_3$. Thus, the results of ab initio calculations could complement the experimental investigations of high pressure transport properties of topological insulators. The experimentally detected increase of carrier density could be related to the effects of the bulk.

1. Introduction
Topological insulators (TI) are the electronic materials that have a bulk band gap like an ordinary insulators, but have conductive states on their edges. Unlike fragile surface states in ordinary metals, the surface states of TIs are topologically protected, i.e. non-magnetic impurities can neither destroy nor impact the topological nature of the surface states. These states are possible due to the combination of strong spin-orbit (SO) interaction and time-reversal symmetry [1, 2]. The best candidate for the study of topological surface states (TSS) is Bi$_2$Se$_3$ thanks to its large bulk insulating gap ($E_G \sim 300$ meV).

TIs could be used for technological applications in spintronics and quantum computing [2]. In order to exploit these materials in electronics, the detailed study of their electronic and transport properties is required. In a recent years, a numerous investigations of different properties of topological insulators, such as conductivity, magnetoresistance and optical properties [3–7] as well as ab initio simulations of TIs compounds [8–10] have been performed.

High-pressure studies are useful to understand the properties of the existing topological insulators and to design new materials because the increase of pressure reduces the interatomic distances and finely tunes materials properties. In order to complement the experimental investigations, which aimed to distinguish surface and bulk contributions into transport properties, ab initio calculations could be of great help.
The present paper is organized as follows: in Section 2 a short overview of experimental results about the transport properties of TIs under the pressure is given; Section 3 is devoted to the details of *ab initio* calculations as well as calculated electronic properties; Section 4 contains discussion and conclusion.

2. Transport properties at high pressure

Bi$_2$Se$_3$ is a narrow band gap semiconductor with a tetradymite crystal structure (space group $R3m - D^{5}$). Its rhombohedral layered structure is formed by quintuple layers (QL), consisted from five hexagonal close-packed atomic sublayers (Se(1)-Bi-Se(2)-Bi-Se(1)), see Fig. 1. Inside the QL the strong covalent bonds are formed, while QLs are linked together by the weak van der Waals interaction.

Results of the electrical transport measurements under the high pressure was reported in the Ref. [3]. The experiments were performed in pressure range from zero to 20.8 GPa at the temperature as low as 20 K. The authors pointed out the increase of resistance in the pressure range from 0 to 8 GPa. The resistivity drops substantially as the pressure increases above the 8 GPa, when structural transition occurs. The carrier density increases by more than two orders of magnitude in the measured pressure range. All measurements were carried out on high mobility, nominally stoichiometric single crystals of Bi$_2$Se$_3$. The substantial increase of carrier density with pressure might be expected to further obscure the surface conduction.

Measurements of the transport and optical properties of Bi$_2$Se$_3$ under hydrostatic pressure as well as *ab initio* calculations of its electronic properties were reported in Ref. [6]. The authors observed the decrease of Hall electron mobility as well as increase of Hall electron concentration for several Bi$_2$Se$_3$ samples with different thicknesses. The corresponding *ab initio* calculations indicated an increasing of direct band gap at Γ point which is coherent with the carried out measurements of optical band gap.

In order to match an experimentally observed increase of carrier density with respect to the pressure with the results of *ab initio* simulations, the density of state (DOS) for bulk and surface Bi$_2$Se$_3$ should be calculated.

3. Calculations

We have performed *ab initio* calculations of the bulk and surface electronic properties of topological insulator Bi$_2$Se$_3$ in the pressure range from 0 to 8 GPa. Calculations have been performed by means of density functional theory (DFT) with exchange-correlation functional PBEsol [11] and with taking into account the spin-orbit interaction, which is realized in the VASP code [12] embedded into MedeA$^\text{®}$ interface. A plane-wave cutoff energy was 256 eV, and $8 \times 8 \times 8$ k-mesh in the Brillouin zone (BZ) for the bulk structures and $8 \times 8 \times 1$ for the surface structures was used. In order to simulate in a right way the hexagonal cell K-meshes was centered at the Γ point. The hydrostatic pressure to the bulk was applied. All atoms in bulk were fully relaxed until forces become less than 0.005 eV/Å.

Band structures and DOS for bulk Bi$_2$Se$_3$ at three different pressures are depicted on the Fig. 2(a). As it can be seen, the increase of pressure leads to the increase of direct band gap at Γ point (which correlates with data presented in Ref. [6]) while the total band gap remains almost constant and equal to 300 meV. Electronic density of states at the bottom of conduction
Figure 2. Calculated band structure and density of state (DOS) near the Fermi level for (a) bulk and (b) 7 QL slab of Bi$_2$Se$_3$ at three different pressures. $P$ and $P_k$ k-points are in a middle on $\Gamma - U$ and $\Gamma - M$ lines respectively. Notation for the BZ points is the same as in Ref. [9].

The calculated band (BCB) slightly increases with respect to pressure due to the decrease of conduction band near the $L$ and $P$ points in BZ, as can be seen from Fig. 2(a).

To simulate effect of the high pressure on the surface states, we used optimized bulk structure at given pressure and made from it the 7 QL slab surrounded by a 20 Å vacuum layer in the direction perpendicular to plane in order to avoid the influence of periodic boundary condition. That is, all interatomic distances as well as lattice parameters in $ab$-plane remains the same as for bulk. In order to make sure in the topological character of surface electronic states, we have determined $Z_2$-topological invariants according to the method described in Ref. [8]. Topological invariant for a surface models was found to be equal to unity for all considered pressures, that confirms the system does indeed have the TSS which remains intact by pressure. However, it was established, that the slabs thinner than 5 QL do not form a TSS, probably due to the strong interaction between top and bottom edges of slab. This fact is coherent to previously reported experimental results [13], where gapped states for the Bi$_2$Se$_3$ films thinner than 5-6 QL were detected. *Ab initio* calculations for similar compound Bi$_2$Te$_3$ indicate that the minimal thickness necessary to form TSS is equal to 5 QL [8].

The calculated band structures along $K - \Gamma - M$ path in hexagonal BZ for a slab of Bi$_2$Se$_3$ consisted of 7 QL under different pressures are presented on the Fig. 2(b). Here we present only
Figure 3. (b) Dirac point energy and (a) velocity at Fermi level along Γ − K and Γ − M directions in BZ for Bi$_2$Se$_3$ in dependence on pressure, calculated for 7 QL slab.

two bands close to the Fermi level and responsible for TSS formation. In opposite to the bulk, one can find a nonzero DOS at Fermi level, that produced by TSS. However, DOS at the BCB has the similar tendency to increase as for a bulk.

Two bands, depicted on the Fig. 2(b), form the so called Dirac cone. The crossing of these bands at Γ point is a Dirac point. Pressure dependence of Dirac point depth with respect to Fermi energy is depicted on the Fig. 3(a). Calculated Dirac point depth at zero pressure (90 meV) well agrees with the experimentally observed one (160 meV) [13]. The dependence of Fermi velocity on pressure is given on the Fig. 3(b). The order of Fermi velocity magnitude is in a good agreement with the experimental value for Bi$_2$Se$_3$ $v_F \simeq 5.0 \times 10^5$ m/s [1] and $v_F \simeq 6.0 \times 10^5$ m/s along Γ − M direction and $v_F \simeq 8.0 \times 10^5$ m/s along Γ − K direction for Bi$_2$Te$_2$Se compound which is similar to the Bi$_2$Se$_3$ [14].

4. Discussion and conclusion

The carrier concentration could be calculated as

$$n = \int_{E_C}^{\infty} f(E)g_C(E) dE,$$

where $E_C$ - energy of the BCB, $f(E)$ - Fermi-Dirac distribution and $g_C(E)$ is density of states for conduction band. That is, DOS at the BCB should make influence on the carrier concentration considerably. The $ab initio$ calculations indicate the increase of this quantity both for a bulk and a slab models. This fact allows us to make an assumption that experimentally observed increase of carrier concentration could be results of a change in bulk electronic properties. On the other hand, authors in Ref. [6] supposed that bulk carrier density decreases, which is in contradiction with our results.

The external pressure does not make any significant influence on the TSS. Indeed, surface states are topologically protected against any perturbations which conserve time-reversal symmetry, such as defects, distortions and non-magnetic impurities. Moreover, TSS are low-sensitive to elastic scattering on impurities as well as scattering on low-energy phonons, as was reported in Ref. [5]. Thus, external pressure stands alongside with other types of disturbances that do not affect the surface states.

On the surface band structure (Fig. 2(b)) one can see the peculiarity at the $P$ point. This k-point corresponds exactly to the $P$ k-point on the bulk band structure. One can suggest that this peculiarity could be the precursor for the insulator-to-metal phase transition of Bi$_2$Se$_3$ [3].
above 8 GPa. Nevertheless, the wave function of this state is distributed in the slab and has no any relationship with TSS.

Calculations indicate that external pressure tends to increase the surface electron velocities at the Fermi level. In its turn, surface electron mobility should significantly depend on the Fermi velocity, because the scattering mechanisms for TSS are rather weak. So, the compression of the Bi$_2$Se$_3$ could be proposed as a mechanism to increase the mobility of surface electron.

In conclusion, we have performed an \textit{ab initio} calculations of band structure and DOS for both bulk and surface of Bi$_2$Se$_3$ with taking into account the spin-orbit interaction. Topologically protected surface states remain intact by pressure. It was established that increase of pressure in the range from 0 to 8 GPa leads to increase of DOS in the bottom of the conduction band, whereas the indirect band gap remains almost constant and equal to $E_g = 300$ meV. Hereby, we suppose, that increase of the Hall electron concentration with respect to external pressure observed in [3, 6] could be caused by this increase of DOS.

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\section*{References}
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