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Electronic Band Structure and Photoemission States of $Bi_{1.96}Mg_{0.04}Se_3$

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We present theoretical band structure calculations and ultraviolet electron photoemission spectroscopy of a topological insulator $Bi_{1.96}Mg_{0.04}Se_3$. Our calculations were based on the first-principles density functional theory with general gradient approximation using Wien2k package with the spin–orbit interaction included by a second-variation method. The $R\bar{3}m$ crystal structure was optimized. In consequence, 4% decrease of volume and 3% decrease of ratio c/a was obtained. This modified structure was multiplied three times in a and b direction in order to place proper amount of Mg. Final crystal structure $P3m1$ with 135 atoms was used for the calculations. As a result metallic band structure was obtained with conduction band extended from –5.6 eV up to 0.16 eV. It composes mostly from Se p states. Comparison of total DOS with ultraviolet photoemission spectrum shows similar features.

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1. Introduction

The materials with full band gap in the bulk but with a gapless dissipationless surface state predicted in systems such as $Bi_{1-x}Sb_x$, Bi_2Se_3, Bi_2Te_3 and Sb_2Te_3 could have significant meaning in spintronic and quantum computational devices. In some materials a superconducting state could be realized by applying pressure e.g. Sb_2Te_3 [1] or by doping e.g. Cu in Bi site in Bi_2Se_3 [2]. In this article we investigate influence of Mg doping in Bi_2Se_3.

2. Computational details

The calculations were done in the Wien2k code [3] based on the density functional theory (DFT) [4, 5] and the generalized gradient approximation (GGA) [6]. Spin–orbit interaction was added using a second-variation method.

As a starting point the rhombohedral crystal structure $R\bar{3}m$ [7] was chosen, where atoms are arranged in five layers Se(1)–Bi–Se(2)–Bi–Se(1). Total energy optimizations of volume and c/a ratio in hexagonal setting led us to 4% decrease of volume and 3% decrease of c/a ratio. In order to place proper amount of Mg this modified structure was multiplied three times in a and b direction. That gave us $Bi_{52/54}Mg_{2/54}Se_{81}$ stoichiometry in $P3m1$ crystal structure with 135 atoms. For final computation 162 k points in a reduced Brillouin zone were chosen. The self-consistent calculations were performed until a charge convergence was better than $0.001e$.

3. Results and their analysis

Calculated band structure shown in Fig. 1 points at that investigated compound has metallic character with the narrow energy gap at high symmetry Γ point. The same gap is isolating in bulk topological insulator [8].

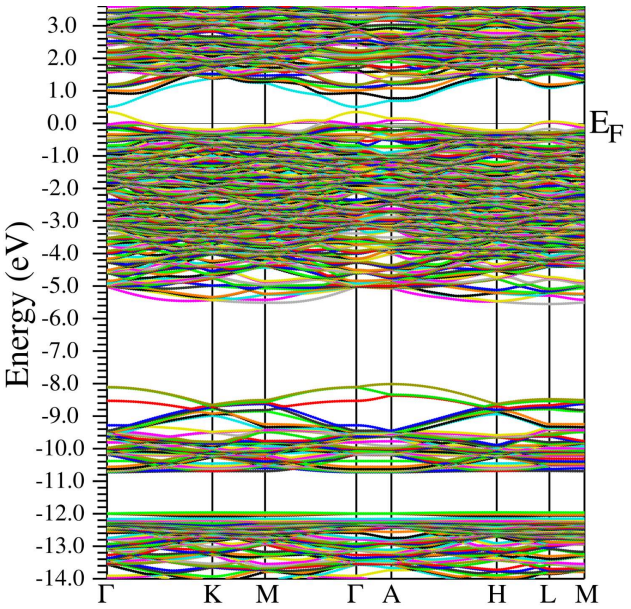

Fig. 1. The calculated band structure.

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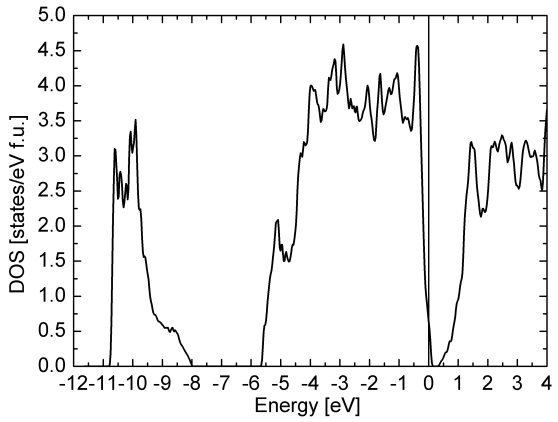

Fig. 2. The calculated total density of states.

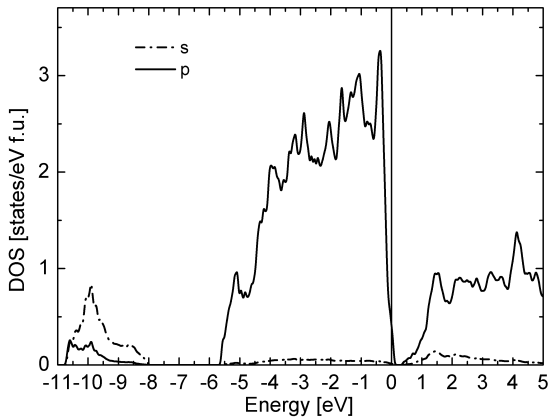

Fig. 3. The calculated partial DOS from Se: dash--dotted line 6s, straight line 6p.

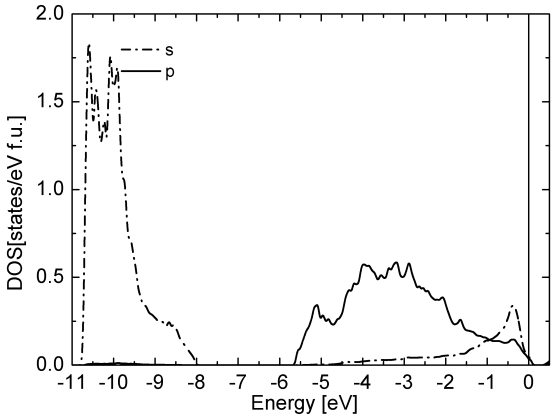

Fig. 4. The calculated partial DOS from Bi: dash--dotted line 6s, straight line 6p.

Doping Mg in this system shifts this gap towards higher energy. This effect is also reflected in total density of state (DOS) (Fig. 2) where valence band DOS decreases from –0.36 eV up to 0.16 eV and energy gap is extended from 0.16 to 0.30 eV relative to Fermi energy (E_F). The valence band extended from –5.7 eV up to 0.16 eV is mostly composed from Se 4p states (Fig. 3) as well as

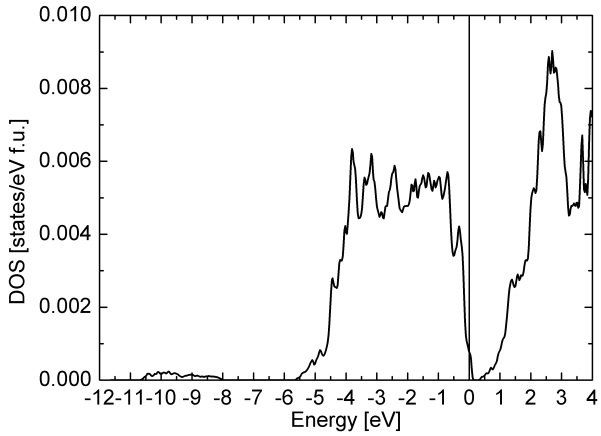

Fig. 5. The calculated partial DOS from Mg.

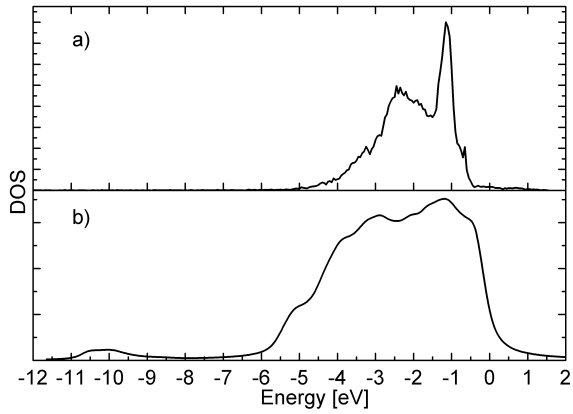

Fig. 6. (a) Ultraviolet photoemission spectrum measured with the photon energy 21.2 eV (He(I) source). (b) Calculated UPS spectrum.

Bi 6p and 6s (Fig. 4). Bi 6p states are mainly on middle of valence band whilst 6s are located at top of it. Bismuth 6s states are from –11 eV to –8 eV. Mg states follows valence band change (Fig. 5). Calculated density of states at the Fermi level is about 0.64 states/ eV f.u. The calculated DOS is in qualitative agreement with the measured ultraviolet photoemission spectrum (Fig. 6) obtained with the photon energy 21.2 eV (He(I) source), for the high-quality $Bi_{1.96}Mg_{0.04}Se_3$ single crystals synthesized by the Bridgman technique.

4. Conclusions

We investigated electronic band structure of Bi_2Se_3 doped with 4% of Mg in site of Bi place. The calculation showed that the doping moved Fermi level downwards into valence bands changing material into a metal. Characteristic gap of the topological insulators was shifted 0.16 eV above Fermi level and their width was 0.14 eV. Valence band was extended from –5.7 eV up to 0.16 eV. The calculated density of states at the Fermi level was around 0.64 states/ eV f.u. The computed DOS was in qualitative agreement with the measured ultraviolet photoemission spectrum (Fig. 6).

Acknowledgments

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