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Chemical bonding and surface interactions in Bi_2Se_3 and Bi_4Se_3

Matthew S. Christian [a], Sarah R. Whittleton [a], Alberto Otero-de-la-Roza [b], Erin R. Johnson [a],*

[a] Chemistry and Chemical Biology, School of Natural Sciences, University of California, Merced, 5200 North Lake Road, Merced, CA 95343, USA
[b] National Institute for Nanotechnology, National Research Council of Canada, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada

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ABSTRACT

Topological insulators are a new class of materials that are insulators in the bulk but have near zero electron transport dissipation behavior on the surface. These surface states are topologically robust (resistant to impurities, defects, and geometry deformations), which makes these materials ideal candidates for a number of technological applications. Well-known three-dimensional topological insulators are bismuth selenide (Bi_2Se_3), which is composed of five-atom-thick layers that interact non-covalently with each other, and Bi–Se alloys resulting from combining these quintuple layers with elemental bismuth bilayers. In this article, we examine the surface sliding and binding energetics of the combinations of quintuple layers and bisumth bilayers found in Bi_2Se_3 and Bi_4Se_3. In addition, we investigate the nature of the chemical bonding in these systems and its relation to the surface energetics.

1. Introduction

Topological insulators (TIs) [1–7] are a new class of materials characterized by metallic surface states that are "topologically protected," that is, resistant to impurities and surface defects, and by being an insulator in the bulk. The mechanism behind the TI properties is similar to the quantum Hall (QH) effect. In the QH state, electrons in a bidimensional material subject to a strong magnetic field perpendicular to the surface are forced to move in quantized orbits, making the material an insulator in the bulk, but conducting on the surface. In these metallic surface states, electrons are forced to move exclusively in one direction, thus preventing backscattering at defects and achieving an almost dissipationless electron flow. Topological insulators show a closely-related behavior, called the quantum spin Hall (QSH) effect. In the QSH state, as in the QH state, dispersionless metallic surface states are present, but a strong external magnetic field is not required, thus making these materials much more interesting from a practical point of view.

The QSH state arises from strong spin–orbit interactions present in TIs. In a TI, the electron spin is locked perpendicular to the crystal momentum, and electrons of different spins are forced to move exclusively in opposite directions on the surface [5]. Backscattering, which would involve a spin-flip, is forbidden due to the presence of time-reversal symmetry. The QSH state is resistant to impurities, surface defects and disorder [5]. In terms of the electronic structure, the signature of a QSH state is the crossing of bands corresponding to surface states, forming what is called a Dirac cone [5]. In addition to being theoretically interesting [3], TIs have great potential for use in future technological applications [4,6] such as, for instance, spintronics [8] and thermoelectrics [9,10].

The strong spin–orbit interaction required for the TI state limits the availability of such materials. Heavy elements, where relativistic effects are important, are usually involved to generate strong spin–orbit coupling. Bi_2Se_3 is the most-studied three-dimensional topological insulator [3,11,12], presenting a Dirac cone composed of surface states and a relatively large band gap in the bulk. Its structure, shown in Fig. 1, consists of ABCABC stacks of five-atom layers, called quintuple layers (QL). The QLs interact with each other primarily via van der Waals forces [13]. Each Bi atom in a QL forms close contacts with six Se atoms, in an octahedral arrangement. The Bi_4Se_3 material is formed by combining QLs and elemental bismuth bilayers (Bi_2) in a 1:1 ratio (Fig. 1), and also presents QSH states and topological insulator behavior [14,15]. The bismuth bilayer is a known 2D topological insulator [16]. Because of the relatively weak inter-layer binding, the QL and Bi_2 can be stacked to form Bi–Se alloys with variable Bi and Se concentration, resulting in extremely long cell lengths in the stacking direction and possibly incommensurate phases [13]. Material properties could be controlled by varying the stoichiometry, though more information about the surface energetics and chemical behavior is needed; [16] this will be addressed in the present work via density-functional theory (DFT).

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* Corresponding author.
E-mail address: ejohnson29@ucmerced.edu (E.R. Johnson).

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Several experimental and theoretical studies on the surface behavior of Bi–Se materials have been conducted in recent years. It is known that the Bi_2Se_3 surface is relatively inert [17] and resistant to oxidation [18,19]. As expected, Bi_2Se_3 cleaves preferentially at the van der Waals inter-QL contacts. It is known experimentally that the geometry and electronic structure of the surface are sensitive to cleavage and show ageing effects, with the Bi concentration increasing over time, although the Se termination can be recovered after annealing [8,20]. He et al., on the other hand, report a preference for a surface Bi termination in Bi_2Se_3 at room temperature that may be attributed to a bismuth bilayer [21], but the Se termination is preferred at low temperatures. The position of the Dirac cone relative to the Fermi level, which is important in the characterization of the TI behavior, is also affected by charge transfer from surface adatoms [20,22].

The nature of the inter-layer interaction was previously explored by Lind et al. [13] using local and semi-local density functionals. However, a functional that includes dispersion attraction is required to accurately describe the inter-layer van der Waals interactions. Liu et al. [23] and Luo et al. [24] used non-local van der Waals density functionals to study the band structure, equilibrium geometry, and exfoliation of Bi_2Se_3, although little attention has been paid to the surface energetics and the nature of the inter-layer chemical bonding. In this work, we apply the exchange-hole dipole (XDM) dispersion model [25], which has been shown to give accurate exfoliation energies for graphite and sublimation energies for molecular crystals [26,27], to study the binding energies and sliding behavior of the QL and Bi_2 surfaces. Furthermore, the nature of the chemical bonding in Bi_2Se_3 and Bi_4Se_3 is relatively unexplored. We present an analysis of the chemical bonding properties in these materials using a range of techniques, including the Quantum Theory of Atoms in Molecules (QTAIM) [28–30], Non-Covalent Interactions (NCI) [31,32], and the Electron Localization Function (ELF) [33,34], to study the atomic charges and inter-layer interactions in these Bi–Se materials.

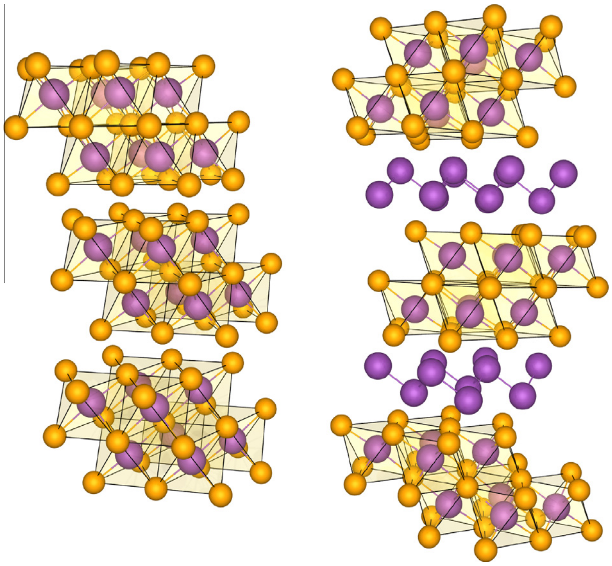

Fig. 1. Structures of bulk Bi_2Se_3 (left) and Bi_4Se_3 (right), showing the quintuple layer (QL) in the former and the QL and intercalated Bi_2 layers in the latter. Bi atoms are represented in violet and Se atoms in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Computational methods

Common density functionals have several well-known shortcomings [35], of which the lack of dispersion interactions and the systematic underestimation of the band gap are particularly relevant to the modeling of topological insulators. In recent years, great progress has been made towards the efficient and accurate modeling of non-covalent interactions by using dispersion-energy functionals [36,37]. These methods capture long-range correlation effects and are coupled to a common density functional (called the base functional) that, in principle, accounts for the non-covalent energy terms other than dispersion.

The structures of the topological insulators considered in this article (Bi_2Se_3 and Bi_4Se_3) consist of stacked QLs and bismuth bilayers that interact with each other via non-covalent interactions (see Fig. 1). In this work, we account for the dispersion energy by using the exchange-hole dipole moment (XDM) model, proposed by Becke and Johnson [25,26,38–47]. In XDM, the total energy from the base functional is supplemented by the dispersion correction,

$$E = E_{\mathrm{base}} + E_{\mathrm{XDM}}, \tag{1}$$

that is calculated using an atom-based pairwise expression:

$$E_{\mathrm{XDM}} = -\sum_{n=6,8,10}\sum_{i<j}\frac{C_{n,ij}f_n(R_{ij})}{R_{ij}^n}. \tag{2}$$

The sum runs over all pairs of atoms in the system, R_{ij} is the distance between atoms i and j, f_n is a damping function that deactivates the dispersion correction at short range, and the $C_{n,ij}$ are the dispersion coefficients for each pairwise interaction. The latter are approximated non-empirically by the electrostatic energy of the electron distributions and their exchange holes in the two interacting atoms. It has been shown that the XDM model offers excellent accuracy for gas-phase [46], as well as condensed-matter, systems [26,27].

In this article, we use the XDM dispersion functional to model the inter-layer interactions in the Bi–Se materials. Our calculations were performed under periodic boundary conditions using the pseudopotentials-plane waves approach as implemented in the Quantum ESPRESSO program [48]. We used B86b [49] exchange coupled with the PBE correlation [50] functional. Both Bi_2Se_3 and Bi_4Se_3 crystallize in the rhombohedral ($R\bar{3}m$) space group and we have used the rhombohedral (primitive) and hexagonal (conventional) cells where convenient. The primitive-cell calculations were carried out using a $4 \times 4 \times 4$ k-point grid while the grid for the hexagonal cell was $4 \times 4 \times 2$. We used the Projector-Augmented Wave method [51] (PAW) and scalar-relativistic pseudopotentials. The cutoff energies were 60 Ry for the plane-waves and 600 Ry for the density.

Regarding the surface energetics, we optimized the bulk geometries and found the equilibrium structures of Bi_2Se_3 and Bi_4Se_3. In Bi_2Se_3, the most stable cleavage occurs between QLs because of their weak non-covalent binding. The Bi_4Se_3 crystal presents alternating QL and bismuth bilayers, so cleavage disrupts van der Waals contacts between a QL and a Bi_2 bilayer.

It is also interesting to examine the non-covalent interactions and energy landscape for sliding, which determines the tribological behavior of these materials. In Bi_2Se_3, we considered two QLs sliding on top of each other, and for Bi_4Se_3 we examine a bismuth bilayer sliding over a QL. These calculations were performed using a supercell with a length of 75 bohr atomic units perpendicular to the slabs. The sliding energetics were computed by displacing the top layer and fixing the x and y atomic coordinates while relaxing the vertical coordinate.