Ab initio studies of adatom- and vacancy-induced band bending in Bi₂Se₃

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We investigate the influence of potassium adsorption and selenium vacancies in the surface layer on the electronic properties of the prototypical topological insulator Bi_2Se_3 . These modifications of the surface give rise to oscillations in the charge density that extend deep into the crystal. They result in a long-ranged potential perpendicular to the surface (also referred to as band bending) and new states in the band structure that are reminiscent of the states of a two-dimensional electron gas. Very similar effects have been observed in several experiments. The reorganization of the charge deep inside the crystal as a reaction to the surface modification constitutes a remarkable property of Bi_2Se_3 and is closely related to its layered structure. The emergence of the long-ranged potential as a direct consequence of the charge reorganization turns out to be a generic property of Bi_2Se_3 . However, calculations without spin-orbit coupling show that the band bending is not related to the nontrivial topological character of Bi_2Se_3 .

DOI: 10.1103/PhysRevB.91.035313

PACS number(s): 73.20.At, 73.20.Hb, 71.70.Ej

I. INTRODUCTION

Topological insulators (TIs) are a recently discovered class of materials that exhibit spin-polarized, topologically protected surface states due to bulk symmetries [1,2]. Bi₂Se₃ was the first both theoretically and experimentally discovered three-dimensional topological insulator [3,4] and still serves as a prototype, due to its simple topological surface band structure with only one Dirac point in the bulk band gap. In several experiments, a temporal evolution of the surface band structure of Bi2Se3 has been observed [5–10]. This "aging effect" is characterized by a down-shift of the Dirac point, the emergence of Rashba-like surface states and the formation of \mathcal{M} -shaped states. This behavior could experimentally be reproduced with different types of intentionally deposited adatoms [5–9,11–13], but it also occurred under UHV conditions [7,10]. These features in the band structure have been interpreted to originate from the formation of a two-dimensional electron gas (2DEG). Such a 2DEG is caused by a potential gradient perpendicular to the surface that confines the electrons and leads to quantized bound states.

However, the details of the potential gradient formation are still under debate [14,15]. Intrinsic electron doping [16], vacancies [12], adsorbates [14] and an increase of the van der Waals (vdW) gap [17,18] have been discussed as possible origins for the band bending. It was shown [16] that intrinsic electron doping can indeed lead to a long-ranged potential that is extended very far into the crystal and results in the experimentally observed changes in the band structure. There has also been a number of theoretical investigations dealing with adatoms or selenium vacancies on Bi_2Se_3 or related compounds [13,14,19–24].

On a microscopic level, the aging effect has been studied by Park *et al.* [14] in the context of potassium adsorption on Bi_2Se_3 . Employing density-functional theory (DFT), the authors have investigated the electronic band structure of K: Bi_2Se_3 as a function of the coupling strength between K and Bi_2Se_3 , which is tuned by the distance between the adatoms and the substrate. Based on these results, Park *et al.* [14] argue that a substantial charge transfer from the adsorbed K atoms to the Bi_2Se_3 substrate gives rise to the observed band bending.

The main goal of our study is to gain understanding of the principal microscopic origins of the band bending. As the band bending occurs in various experimental conditions, its origin should be related to generic properties of Bi₂Se₃.

Motivated by the experiments cited above, we investigate the influences of potassium adsorption and of selenium vacancies in the surface. Potassium serves as a prototype adsorbate. To further ensure that the obtained results are not specific to potassium, we also investigate selenium vacancies in the surface layer. Vacancies have been discussed as possible origin of the band bending [12], but as yet there are no theoretical works showing that vacancies can lead to band bending. Although these two perturbations of the ideal surface are quite different, they lead to the same qualitative effects.

Up to now, the spatial structure of the charge density inside the crystal has not been taken into account in an explanation of the band bending. In this work, we investigate in detail the charge transfer ΔQ into the crystal and the changes in the charge density $\Delta \rho(\mathbf{r})$ inside the crystal that arise upon a distinct perturbation, e.g., adatoms or vacancies, of the pristine surface of Bi₂Se₃. This is motivated by the observation that a similar amount of charge transfer (ΔQ) as in K:Bi₂Se₃ occurs, e.g., for the adsorption of potassium on Si(001)-(2 × 1). In that case, however, no long-ranged potential inside the Si substrate appears [25].

We will outline that considering solely the amount of shifted charge is not sufficient to explain the formation of the longranged potential. A reorganization of the charge distribution inside the substrate plays a crucial role and is indispensable in an explanation of the band bending. Bi₂Se₃ consists of a periodic arrangement of quintuple layers (QLs), which are formed by layers of Se and Bi atoms, respectively, in the sequence Se-Bi-Se-Bi-Se. We will show on the basis of DFT calculations that the resulting reorganization of the charges is related to the layered structure of the crystal in combination with its special screening properties. The formation of the long-ranged potential is a direct consequence of the changes in the charge density.

1098-0121/2015/91(3)/035313(13)

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One might suppose that the peculiar charge redistribution inside Bi_2Se_3 may result from its topological-insulator nature. However, one can easily turn Bi_2Se_3 into a conventional semiconductor by switching off the spin-orbit coupling (SOC) [2]. In such a calculation, Bi_2Se_3 still exhibits the same longranged charge redistribution (see below), which proves that the topological nature of Bi_2Se_3 is *not* responsible for the band bending.

First, we consider the adsorption of K on Bi₂Se₃ and discuss the resulting band bending and its influence on the band structure for various potassium coverages. In this context, we analyze whether the effects in the electronic structure are specific to K adsorption or are of more general nature. To this end, we carry out a calculation for a Bi2Se3 surface with an additional model potential that simulates the band bending. A comparison with these results enables us to differentiate between distinct origins of the adsorption-induced changes in the band structure. Secondly, we carefully investigate the charge density of the K-covered slab. By scrutinizing the origins of the observed charge density, we examine the details of the formation of the long-ranged potential and how this is related to the layered structure and the element-specific nature of Bi₂Se₃. Finally, we show that selenium vacancies in the surface layer give rise to qualitatively the same effects as K adsorption.

The paper is organized as follows. In Sec. II, we describe technical details of our calculations. Section III deals mainly with the effect of K adsorption and the resulting long-ranged potential on the band structure of Bi₂Se₃. The main results of this paper are presented in Sec. IV in which we investigate the spatial structure of the charge density inside the crystal and how this leads to the observed band bending. Emphasis is laid on the role of the layered structure of Bi₂Se₃. Results for selenium vacancies in the surface layer are discussed in Sec. V. We close with a summary of the main points (Sec. VI).

II. METHODS AND COMPUTATIONAL DETAILS

We perform calculations within the framework of densityfunctional theory and use the local density approximation (LDA) [26]. To this end, we use a code which has been developed in our group [27,28]. The electronic wave functions are represented by a basis set of Gaussian orbitals with s, p, d, and s^* symmetry [29] that are localized at the atomic positions. We use nonlocal norm-conserving *ab initio* pseudopotentials [30] in the separable Kleinman-Bylander form [31] and nonlinear partial core corrections [32] are employed for potassium. Scalar relativistic corrections as well as SOC are included in the pseudopotentials [28] and the surface is treated within the supercell approach. Brillouin zone (BZ) integrations are performed using a $\overline{\Gamma}$ -centered Monkhorst-Pack mesh [33] of size $12 \times 12 \times 1$, which corresponds to 19 k points in the irreducible part of the hexagonal BZ. In structural optimizations, forces are converged to 1×10^{-4} Ry/ a_0 (with the Bohr radius a_0).

To ensure a consistent description of the K adsorption, we optimize the bulk lattice parameters of Bi₂Se₃ within LDA and find a = 4.14 Å and c = 27.61 Å for the hexagonal lattice constants. The internal parameters describing the positions of the atoms inside the unit cell are v = 0.2090 and $\mu =$



FIG. 1. (Color online) Top view of the Bi₂Se₃(111) surface. The three topmost layers are shown and possible adsorption sites for adatoms are indicated.

0.4008 (see Ref. [34] for definition). Our results agree well with experimentally determined values, e.g., Ref. [35] gives the values a = 4.1355 Å, c = 28.615 Å, v = 0.2109, and $\mu = 0.4006$.

III. POTASSIUM ADSORPTION AND ITS EFFECTS ON THE BAND STRUCTURE

A. Adsorption geometry of potassium on Bi₂Se₃

Five conceivable adsorption sites for adatoms on the Bi₂Se₃ surface are depicted in Fig. 1. The H site is above the atom of the third layer of the crystal. In continuation of the crystal, the Se atoms of the next atomic layer would occupy the H sites. We calculate the vertical atomic distances d_z of the K atoms from the selenium surface layer and binding energies E_B for potassium adatoms on each of these sites in the case of one adatom per 1×1 unit cell of Bi₂Se₃ [one monolayer (ML) coverage] and in the case of one adatom per $\sqrt{3} \times \sqrt{3}$ unit cell of Bi₂Se₃ (1/3 ML coverage). The binding energy is defined as

$$E_B := -(E^{\mathrm{K-covered\,slab}} - E^{\mathrm{pristine\,slab}} - E^{\mathrm{K}}), \qquad (1)$$

where E^X denotes the total energy of system X. All three calculations (for X=K-covered slab, pristine slab, and K) are performed with the same basis set for the wave functions in order to avoid the basis set superposition error [36]. The adsorption process was studied on a Bi2Se3 slab of 3 QL thickness (25.27 Å in total) with K atoms on both sides. The results are listed in Table I. The presented numbers are obtained without considering relaxation of the Bi₂Se₃ surface layers. We have checked that structural optimization of these layers results in minor shifts of the atomic positions in z direction and no surface reconstruction is observed. Here, we optimize only the K positions because we want to investigate the principal effect of the adatoms. A comparison of the potentials (Sec. III C) or charge densities (Sec. IV A) of the Bi₂Se₃ surface with and without adatoms requires that the surface structure is the same to avoid artefacts from Bi₂Se₃ relaxation.

TABLE I. Atomic distances d_z and binding energies E_B for potassium on Bi₂Se₃ at the different possible sites H, C, and T (see Fig. 1 for explanation). Adsorption in positions B and D is unstable.

Site	Н	С	Т		
	1 monolayer coverage				
d_z (Å)	2.43	2.51	3.30		
E_B (eV)	1.38	1.31			
	1/3 monolayer coverage				
d_z (Å)	2.15	2.23	3.12		
E_B (eV)	3.16	3.02	2.01		

It turns out that the B and D sites are unstable for both investigated coverages. The H site is the favored adsorption site in both cases, but it is energetically only slightly preferred over the C site, and the distance to the surface is also comparable. The binding energies are much larger for 1/3 ML coverage than for 1 ML coverage and the binding lengths become shorter, accordingly. This can be explained by the fact that in the one ML case the potassium atoms show strong binding to each other, thus forming an atomic layer, whereas in the 1/3 ML case the K atoms can be regarded as nearly isolated and have only a very weak inter-atomic binding and are therefore more strongly bound to the crystal surface. Reference [14] also gives the H site as the favorable adsorption position.

B. Band structures

We now discuss the band structure of Bi_2Se_3 with adsorbed potassium in comparison to the band structure of the pristine surface. For the pristine surface and the surface with one ML coverage, we use Bi_2Se_3 slabs of 13 QL thickness. The calculations for 1/3 ML coverage are performed with a 7 QL slab because of the high computational cost. We use a symmetric setup with K atoms on both surfaces of the slab. Figure 2 shows the band structure for potassium adsorbed on the H site. We will only discuss this case in the following because it is the energetically most favorable one.

The band structure of the pristine surface is in good agreement with other band structures for Bi₂Se₃ from the literature [20,22,37,38]. Slight differences occur because we use our LDA-optimized lattice parameters whereas most other studies have been performed with experimental lattice parameters. The choice of the lattice parameters influences for example the shape of the band gap edges [39]. The bulk band gap is closed by the spin-polarized topological surface state (TSS). The Rashba-component of the spin expectation value is indicated in Fig. 2 by blue (red) points for positive (negative) values. The Fermi level E_F is 0.01 eV below the valence band maximum. In the valence band pocket around $\overline{\Gamma}$ (between -1.1 and -0.5 eV), there is another spin-polarized surface state. This state also occurs for the topological insulator Sb₂Te₃ and has been investigated in detail in Ref. [40].



FIG. 2. (Color online) The band structures of a pristine slab (left) and of K-covered Bi₂Se₃ slabs with 1 ML (middle) and 1/3 ML coverage (right) are shown. The gray areas show the projected bulk band structure. Red (blue) dots indicate a negative (positive) Rashba component of the spin expectation value. For the definition of the Rashba-component P_{\perp} at a given wave vector \mathbf{k}_0 , please see the inset in the left panel. The size of the dots is proportional to the absolute value of the Rashba component. The bands from the upper and lower surfaces of the slab have opposite Rashba components. Here, only the values of the bands from the upper surface are shown. This applies to all figures. In the middle and right panels, green lines indicate states that are predominantly located on the potassium atoms, as resulting from a Mulliken population analysis. The arrows mark the upper part of the modified TSS (see text for explanation). The thickness of the lines is proportional to the Mulliken population. The valence-band maximum (VBM) of the projected bulk band structure is taken as the zero of the energy scale.

General striking features of the Bi₂Se₃ surface band structure are the quite big pockets, especially in the unoccupied part of the band structure. At $E \approx 1.4$ eV, a "second Dirac point" is visible at $\overline{\Gamma}$. The existence of this state depends on the lattice parameters and has been described in the literature [41,42].

K-adsorption gives rise to a number of spin-polarized surface states that do not appear on a pristine surface (see middle panel of Fig. 2). In order to unravel the band structure of the K-covered slab, we perform a Mulliken population analysis [43] of the bands and vary the K-slab distance (not shown here). For large distances, the resulting band structure becomes the superposition of the band structures of a pristine Bi₂Se₃ slab and an isolated monolayer of potassium. The evolution of the bands from this noninteracting case to the band structure in the middle panel of Fig. 2 can be tracked for the intermediate distances. This analysis together with the study of a model potential (Sec. III D) leads to the following interpretation of the band structure in Fig. 2 (middle panel).

Two distinct origins of the surface states in the band structure of the K-covered surface can be distinguished: The first mechanism is an adsorbate-specific change of the effective potential near the surface, due to the binding of the adatoms to the surface atoms. The second mechanism is a universal feature of Bi2Se3 that occurs for various adsorbates as well as for vacancies in the surface layer (see Sec. V): The emergence of a long-ranged potential perpendicular to the surface, often referred to as band bending [44]. In Sec. III C, we explicitly show that a long-ranged potential perpendicular to the surface comes up in Bi₂Se₃ upon K adsorption. In Sec. III D, we use a simple model to show how a band structure looks with pure band bending in the absence of adsorbate-specific states. This allows us to clearly identify the band bending-induced states in the band structures of the K-covered slabs. That analysis supports the assertion we make about band bending-induced states in this section.

We begin the discussion of the band structure of the K-covered slab by describing the modification of the surface states of the pristine surface upon K adsorption. The TSS undergoes a shift to lower energies, with the Dirac point itself being shifted from E = -0.24 eV on the pristine surface to E = -0.93 eV on the K-covered surface. The lower part of the modified TSS [45] is marked by the yellow box labeled "A" in the middle panel of Fig. 2. The part of the TSS with negative Rashba-component (red points) hybridizes with K-induced surface states and therefore a "gap" is opened for the TSS, i.e., the modified TSS in box A is not connected with the conduction bands. The states in the projected bulk band gap marked by arrows are relics of the original TSS and can be regarded as the continuation of the upper bands in box A. The Mulliken analysis of these bands shows contributions from potassium as well as from the uppermost surface layers.

The surface state that occurred in the valence band pocket on the pristine surface has been shifted to lower energies and is not visible anymore on the K-covered surface. The down-shifts of the TSS and of the bands in the valence band pocket can be attributed to the long-ranged surface potential (see below).

We now discuss the potassium-specific states which are marked by green lines in the middle panel of Fig. 2. They range from $E \approx 1$ eV near \bar{K} to $E \approx -0.43$ eV at $\bar{\Gamma}$ (close above the magenta box labeled "B"), bridging the bulk band gap. Between $\overline{\Gamma}$ and \overline{M} , the spin-polarized bands that arrive at \overline{M} just above E_F and at E = 1.39 eV, respectively, show significant potassium contributions. The band structure of a free-standing K monolayer is nearly parabolic. Upon adsorption on the Bi₂Se₃ surface, the parabola splits due to the SOC and its dispersion gets reduced due to the interaction with the slab. Close to $\overline{\Gamma}$, the potassium-states show a large spin polarization.

In addition to all those states, there is a number of further states in the band structure of the K-covered slab that are absent on the pristine surface. The emergence of these further states can be explained in the picture of band bending and is not K-specific. Band bending can be understood in terms of an effective potential, which is lowered (or raised) at the surface compared with the potential in the bulk. A lowered potential confines the electrons at the surface, and they can be described as a 2DEG. Similar to the Rashba effect, the SOC leads to a splitting of spin-degenerate states and gives rise to spin polarization. The above described downshifts of the TSS and of the band in the valence band pocket also stem from such a lowered potential.

The \mathcal{M} -shaped pair of spin-polarized states in box B in Fig. 2 has been "pulled down" from the uppermost valence bands by the band bending. It resembles the \mathcal{M} -shaped bands observed in several experiments [6,10,16,46] and calculations [14,16,17] with different kinds of modifications of the ideal Bi₂Se₃ surface. The band with positive Rashba-component is energetically above the band with negative Rashba-component, in contrast to the ordering in the TSS.

Below the conduction band minimum (CBM), at least two pairs of spin-polarized states have emerged in the bulk band gap, one pair at $E \approx 0$ eV around $\overline{\Gamma}$ and the other one just below the CBM at $E \approx 0.18$ eV. These states have been pulled down from the conduction band edge due to band bending. Their dispersion and spin polarization is similar to the spinsplit parabolas of free electrons in the Rashba effect. Therefore, we name these states "Rashba-like states" in the following. In our case, the Rashba-like states do not show strictly parabolic dispersion since they reflect the dispersion of the conduction band edge.

At higher energies, new states, which are marked by box C (in the middle panel of Fig. 2), are also visible in the conduction band pocket. The lower pair of spin-polarized states reflects the W-shaped dispersion of the upper edge of the pocket from which it emerged. The upper pair of states has been pulled down from parabolic bulk bands at $E \approx 1.2$ eV.

Effects that we attribute to the band bending (down-shift of the TSS, emergence of \mathcal{M} -shaped bands, and the Rashba-like bands) have been observed for adsorbate-covered Bi₂Se₃ surfaces, both experimentally [6,10,16,46] and theoretically [14]. Here, we point out that band bending not only induces changes around the Fermi energy, but also in the whole unoccupied part of the band structure, e.g., the states in box C. It generally leads to the emergence of new bands below the bulk band edges, because the corresponding wave functions are localized close to the surface and are thus influenced by the lowered potential. The aforementioned pockets in the unoccupied part of the band structure facilitate the occurrence of spin-polarized surface states below the band edges.

The right panel of Fig. 2 shows the band structure for 1/3 ML K-coverage. We use the same scale in all panels, so one length unit in **k** space is the same in all panels. The $\sqrt{3} \times \sqrt{3}$ unit cell is rotated by 30° with respect to the 1 × 1 unit cell, therefore the $\bar{\Gamma}\tilde{M}$ ($\bar{\Gamma}\tilde{K}$) direction corresponds to the $\bar{\Gamma}\tilde{K}$ ($\bar{\Gamma}\tilde{M}$) direction, with \tilde{K} (\tilde{M}) denoting the $\bar{K}(\bar{M})$ point of the $\sqrt{3} \times \sqrt{3}$ BZ. The enlarged unit cell leads to a smaller BZ and thus to back-folding of the bulk bands. Therefore the size of the pockets of the projected bulk band structure is reduced in the $\sqrt{3} \times \sqrt{3}$ unit cell. However, the area around $\bar{\Gamma}$ between -0.5 and 1 eV remains nearly unaffected and can be well compared with the 1 × 1 band structure.

For the lower K-coverage of 1/3 ML, the band structure again changes significantly, compared to the case of 1 ML K coverage. The TSS is located at lower energy than on the pristine surface but at higher energy than on the fully K-covered surface. The Dirac point is shifted to E = -0.7 eV into the region of projected bulk bands; only the upper part of the TSS with approximately linear dispersion and negative Rashba-component can be seen, emerging from the bulk valence bands, in the right panel of Fig. 2. We emphasize that in this case, as well as for one ML K coverage, it is actually not meaningful to use the term "Dirac point," as there is no crossing of bands with linear dispersion. Only a comparison with the pristine surface can justify this name.

The K-dominated states are located at $E \approx 0.65$ eV in the conduction band pocket and do not hybridize with the TSS. Due to the increased distance between the K atoms, the dispersion is now much flatter than for one ML coverage. The 2DEG-like states from box C in the middle panel of Fig. 2 are shifted to higher energies, compared to one ML coverage. The size of the valence band pocket is reduced due to the back-folding of bulk bands, and no \mathcal{M} -shaped bands are visible for 1/3 ML K coverage. Apart from this, the band bending effects are also present for 1/3 ML K coverage: The down-shifted TSS, Rashba-like bands below the CBM and a surface state in the conduction band pocket can be identified.

As a concluding remark to the discussion of the band structures we note that the bulk band gap is closed by surface states for all three coverages (0, 1, and 1/3 ML) regarded. This, together with the observation that there is always an odd number of crossings of surface states with a line of constant energy in the bulk band gap, is a manifestation of the nontrivial topological character of the band structure of Bi₂Se₃.

C. Slab potentials

The upper part of Fig. 3 shows the laterally averaged effective potentials

$$V(z) := \frac{1}{A} \int_{A} V_{\text{eff}}(\mathbf{r}) \, dx \, dy \tag{2}$$

of a pristine and a K-covered slab. The integral is over the unit cell in xy direction with area A. Close to the surface (z = 0) and in the vacuum (z > 0), they distinctly differ, while deep in the bulk they nearly coincide. At z = 10 Å, V(z) = 5.72 eV (2.88 eV for the K-covered surface) denotes the work function of the surface. Apparently, it is significantly reduced by K adsorption [47].



FIG. 3. (Color online) The upper part shows the averaged effective potentials V(z) of a 13 QL slab with and without adsorbed K. V(z) = 0 represents the Fermi energy. The lower part shows the difference $V_{\text{diff}}(z)$ of these two potentials. For comparison, $V_{\text{diff}}(z)$ for K adsorbed on Si(001) is also shown. Vertical dotted lines indicate the midpoints of the vdW gaps between two neighboring quintuple layers. z = 0 is the position of the outermost selenium layer of the slab. The label "K" indicates the position of the K layer. The inset shows the same data on an enlarged energy scale.

To see the change in V(z) more clearly, we plot the difference

$$V_{\text{diff}}(z) := V^{\text{Slab}+\text{K}}(z) - V^{\text{Slab}}(z)$$
(3)

in the lower part of Fig. 3. This plot reveals the abovementioned lowering of the potential perpendicular to the surface. For comparison, the dashed curve shows the same quantity for the case of a K-covered Si(001) surface [48]. For this "ordinary" semiconductor, $V_{\text{diff}}(z)$ decays to zero within a few angstroms, while for Bi_2Se_3 we have $|V_{diff}| > 10$ meV even 40 Å deep in the bulk. The comparison with K:Si(001) also demonstrates that this unusual behavior has its origin in the properties of the crystal and not in the properties of the adsorbate. In addition, we emphasize that the long-ranged potential is *not* related to the topological character of Bi₂Se₃ or the TSS, respectively. Calculations without SOC yield very similar, equally long-ranged potentials. A careful look at the details of $V_{\text{diff}}(z)$ (see inset of Fig. 3) already points out a possible connection with the layered structure of Bi₂Se₃: In the vdW gaps (marked by dotted vertical lines), the slope of $V_{\text{diff}}(z)$ is steeper than inside a QL. The relation between the layered structure and the long-ranged potential will be further analyzed in Sec. IV B.

Let us briefly compare our calculated $V_{\text{diff}}(z)$ to other proposals for the band bending potential from the literature. In Ref. [6], a constant charge density (with a nonzero net charge) close to the surface was assumed. First, the potential resulting from this charge density was calculated by means of the Poisson equation. Then, the Schrödinger equation with this potential was solved. The free parameters in this model were



FIG. 4. (Color online) The model potential $V_M(z)$ in comparison with $V_{\text{diff}}(z)$ from Fig. 3 and the resulting band structure (see text for details of the calculation).

used to achieve the best agreement of the resulting energies with experimental data. In Ref. [16], a more sophisticated ansatz is taken for the solution of the Poisson equation. Constant donor and acceptor densities as well as electron and hole densities resulting from a $\mathbf{k} \cdot \mathbf{p}$ -Hamiltonian are taken into account to describe the charge density. The resulting potential is added to the onsite terms of a tight-binding Hamiltonian. Both approaches yield band bending potentials extending over $\approx 150-200$ Å.

In Ref. [14], an exponentially decaying potential $V(z) = -V_B e^{z/w}$ was added to a tight-binding Hamiltonian. Based on DFT results, w = 15 Å and $V_B \le 1.5$ eV were chosen. The potential resulting from our calculations has a depth of 0.8 eV and extends over roughly 40 Å (cf. Figs. 3 and 4 and the discussion in Sec. III D).

The two different approaches have the following characteristics: Assuming an additional charge density and fixing the potential by the measured shift of the Dirac point leads to very long-ranged potentials with little amplitude (Refs. [6, 16]). A microscopic description of the processes evoked by adatoms on the surface (calculated within DFT) leads to a band bending potential on a shorter length scale but with stronger amplitude (Ref. [14] and our present work). The approaches from Refs. [6, 16] lack a microscopic explanation for the origin of the charge density leading to the potential. The calculations from Ref. [14] and this work, however, assume ideal crystals without defects that could lead to free charge carriers that would result in longer ranged potentials.

D. Calculations with a model potential

We will now briefly discuss the effects resulting from the long-ranged behavior (perpendicular to the surface) of the potential. To this end, we first perform a self-consistent LDA calculation for the pristine slab, yielding the potential $V_{\text{LDA}}(\mathbf{r})$. Then we add a z-dependent model potential $V_M(z)$ [simulating $V_{\text{diff}}(z)$ like the one of Fig. 3] to $V_{\text{LDA}}(\mathbf{r})$ and finally calculate the band structure of the resulting potential $V_{\text{res}}(\mathbf{r}) = V_{\text{LDA}}(\mathbf{r}) + V_M(z)$. As model potential we choose a simple Morse potential [49] $V_M(z)$ with

$$V_M(z) = V_0(1 - e^{-\gamma(z - z_0)})^2 - V_0.$$
(4)

The minimum value of $V_M(z)$ is given by $V_M(z_0) = -V_0$ and the parameter γ controls how far the potential is extended into the crystal. The surface selenium layer is chosen as the position of z_0 . In analogy with the symmetric slab structure as discussed in Sec. III B, the Morse potential is added on both surfaces of the slab. Performing these calculations for different parameters (e.g., increasing V_0) allows us to comprehend the evolution of the band structure of pristine Bi₂Se₃ for an increasing surface potential.

With $V_0 = 0.8$ eV and $\gamma = 0.09/a_0$, $V_M(z)$ closely resembles the potential difference $V_{\text{diff}}(z)$ from Fig. 3 (see Fig. 4), therefore it is possible to quantitatively compare the band structures from Figs. 2 (middle panel) and 4.

On the pristine surface, the TSS is inside the bulk band gap and the Dirac point is located at E = -0.24 eV (see again the left panel of Fig. 2). The model potential leads to a down-shift of the Dirac point to E = -0.84 eV (see Fig. 4). The other spin-polarized state in the valence band pocket of the pristine surface is also shifted to lower energies and is not visible in Fig. 4. Obviously, the model potential leads to a number of spin-polarized surface states that do not exist on the pristine surface. In the valence band pocket around $\overline{\Gamma}$, an \mathcal{M} -shaped state with two branches of negative (red points) and positive (blue points) Rashba-component is visible between E = -0.65 and -0.45 eV. Below the CBM, a series of at least two pairs of Rashba-like states is observed. New states have also emerged in the conduction band pocket around $\overline{\Gamma}$: The W-shaped pair of states between 0.5 and 0.75 eV has been pulled down from the upper edge of the pocket, while the pair of states disperging from 0.8 eV to higher energies comes from parabolic bulk bands. In general, the model potential leads to the emergence of spin-polarized surface states below every band edge, also for higher energies that are not shown in Fig. 4.

The calculated band structure with the simulated band bending thus shows all the features of the band structure of the fully K-covered slab (Fig. 2, middle panel), except for the adsorbate-specific potassium-dominated states. These findings justify the statement made above, i.e., that the differences between surface states with and without K adsorption originate from two different sources: From the adsorbate-specific shortrange part of the potential and from the long-ranged part of the potential ("band bending").

IV. MICROSCOPIC ORIGIN OF THE LONG-RANGED POTENTIAL

The details in the spatial structure of the charge density inside the crystal are of great importance for an understanding of the band bending effect in Bi_2Se_3 . In Sec. IV A, the special properties of the charge density in Bi_2Se_3 and their consequences for the resulting potential are demonstrated. We identify the layered structure of the material as a crucial ingredient for the long-ranged potential in Sec. IV B.

Let us first give definitions of the terms used in the following discussion. We compute the difference $\Delta \rho(\mathbf{r})$ of the charge densities $\rho(\mathbf{r})$ of the K-covered slab and of the two isolated subsystems (a pristine slab and a freestanding K monolayer):

$$\Delta \rho(\mathbf{r}) := \rho^{\text{Slab}+\text{K}}(\mathbf{r}) - [\rho^{\text{Slab}}(\mathbf{r}) + \rho^{\text{K}}(\mathbf{r})].$$
(5)

Based on this, we define the laterally averaged charge density by

$$\rho(z) := \frac{1}{A} \int_{A} \rho(\mathbf{r}) \, dx \, dy. \tag{6}$$

 $\Delta \rho(z)$ shows the changes in the charge density when the adsorbate interacts with the slab (see Fig. 5). Following Ref. [14], the amount of charge ΔQ that is transferred from



FIG. 5. (Color online) The upper part shows $\Delta \rho(z)$ for K-covered Bi₂Se₃ as defined in Eq. (5). The colored vertical lines mark different points z_0 for which we compute $\rho_c(z)$ (see text for further explanation). The lower part shows the Coulomb potential of $\rho_c(z)$ for different z_0 in the corresponding colors. The black line shows the potential of the original $\Delta \rho(z)$ of K-covered Bi₂Se₃. The dotted lines mark the QLs, the surface, and the K position as in Fig. 3.

TABLE II. Charge transfers ΔQ as calculated from Eq. (7) for the various systems treated in this work. ΔQ is given in electrons per surface unit cell, or, equivalently, per adatom. K:Si refers to K:Si(001) in the adsorption geometry that we also use for K:vdW-Si (see Sec. IV B for details). A positive value indicates the transfer of electrons into the subtrate.

	K:Bi ₂ Se ₃	K:Bi ₂ Se ₃ ^a	K:BiSe	K:Si	K:vdW-Si
ΔQ	0.110	0.112	0.119	0.094	0.133
^a From	Ref. [14].				

the adlayer into the crystal is defined by

$$\Delta Q := A \cdot \int_{-\infty}^{K/2} \Delta \rho(z) dz, \tag{7}$$

where K/2 denotes half the distance between the substrate $(z \le 0)$ and the adlayer (z = K). The choice of K/2 as lower limit of the integral is somewhat arbitrary but reasonable.

The number ΔQ gives no information about the distribution of the transferred charge within the crystal. This redistribution can equally well happen within a few Å or within a few hundred nanometers. Therefore two quantities have to be distinguished:

(1) The charge transfer ΔQ . This number quantifies a transfer of charge from an adlayer towards the crystal. However, no information is contained in ΔQ about the reaction of the charge density inside the crystal.

(2) The charge redistribution $\Delta \rho(\mathbf{r})$ [or $\Delta \rho(z)$, respectively]. This quantity describes the rearrangement of the charge *inside* the crystal. Note that this quantity is not necessarily zero in a certain interval I within the crystal, even if $\int_{I} \Delta \rho(z) dz = 0$ (cf. Fig. 5 and the discussion below).

We find very similar charge transfers ΔQ for all systems treated in this work (cf. Table II). Yet, we observe completely different behaviors of $\Delta \rho(z)$ in these systems. The implications for the formation of a long-ranged potential will be pointed out in the following.

A. Charge density of K:Bi₂Se₃

In this section, we discuss the microscopic origin of the long-ranged potential. In particular, we demonstrate its relationship with long-ranged charge density effects.

For Bi₂Se₃, $\Delta \rho(z)$ shows a periodicity related to the QL structure of the crystal, which is, however, modified by a *z*-dependent amplitude function a(z) decaying into the bulk, i.e.,

$$\Delta \rho(z) = f(z)a(z). \tag{8}$$

To substantiate that SOC is *not* involved in the band bending process, we also perform calculations without SOC, rendering the system topologically trivial [2]. For one ML of K on Bi₂Se₃, we find

$$a(z) \approx \exp(z \, 0.08/\text{\AA})$$
 with SOC, (9)

$$a(z) \approx \exp(z \, 0.06/\text{\AA})$$
 without SOC. (10)

To reveal the underlying periodic function f(z), we show in Fig. 6 the "decay-corrected" quantity $f(z) = \Delta \rho(z)/a(z)$. The curves with and without SOC are nearly identical. They only differ noticeably within the first QL. The calculations with and



FIG. 6. (Color online) The "decay-corrected" charge density difference f(z) (see text for explanation) for K-covered Bi₂Se₃ with and without SOC. Dotted vertical lines mark the midpoints of the vdW gaps. The underlying periodic structure in $\Delta \rho(z)$ for z < -8 Å is nicely revealed.

without SOC yield equally long-ranged potentials. Therefore the band bending is not related to the nontrivial topological character of Bi₂Se₃.

Except for the first QL, the various amplitudes of f(z) are nearly the same in every QL. Deviations from a perfectly periodic behavior result from the approximation we make for a(z). Figure 6 shows that [apart from the damping a(z)] the main feature of $\Delta \rho(z)$ is charge accumulation and depletion at the contiguous edges of two quintuple layers, i.e., there are dipoles in the vdW gaps.

The most prominent feature of $\Delta \rho(z)$ in Fig. 5 is a large shift of charge from the potassium layer to the surface. This can be attributed to the binding of the adsorbate to the surface. Thus a dipole is formed at the surface which mainly leads to the reduction of the work function, because the Coulomb potential V_{coul} of a surface dipole is (approximately) a step function. In addition to this shift of charge, oscillations in $\Delta \rho(z)$ inside the crystal are visible in Fig. 5.

We show now that the band bending in Bi₂Se₃ can only be explained when the oscillations in $\Delta \rho(z)$ are taken into account. It is not sufficient to consider merely the surface dipole. The rearrangement of the charges deeper inside the crystal plays a major role in the band bending process. To investigate the effect of the oscillations, we define a one-dimensional cutoff charge density $\rho_c(z)$ with

$$\rho_c(z) := \begin{cases} \Delta \rho(z) & \text{if } z \ge z_0 \\ 0 & \text{else} \end{cases}.$$
(11)

This definition means that with ρ_c we investigate the influence of $\Delta \rho$ on V_{coul} only up to a certain distance $|z_0|$ from the surface, while $\Delta \rho$ deeper in the bulk (i.e., $z < z_0$) is switched off. The cutoff points z_0 have to be chosen such that charge neutrality is preserved (because we want to model the difference in charge density between charge neutral systems) [50]. The z_0 for which charge neutrality is preserved are the zeros of the integrated charge density, i.e., $\int_{z_0}^{\infty} \Delta \rho(z) dz = 0$.

Our results (see Fig. 5) show that the oscillations of $\Delta \rho(z)$ inside the crystal are the origin of the band bending. They give rise to a potential that is constant in the range $z < z_0$ [with $\rho_c(z) = 0$], while it is lowered towards the surface (for $z > z_0$). There is an obvious connection between the choice of z_0 and the amount of band bending: For cutoff points z_0 deeper in the crystal, the band bending becomes "stronger," i.e., the value |V(0)| increases and the range with $V(z) \neq 0$ becomes

farther extended into the crystal. Therefore only computing the amount ΔQ of charge transferred from the adsorbate to the substrate [see Eq. (7) for definition] is not sufficient to explain the band bending, because this ΔQ is the same for all curves in Fig. 5.

The comparison between, e.g., the blue and magenta curves in Fig. 5 nicely illustrates a crucial reason for the band bending in Bi₂Se₃: The difference in $\rho_c(z)$ between these two curves is just one dipole in a vdW gap that is formed by the charge accumulation and depletion at the edges of two adjacent quintuple layers. This dipole leads to a potential difference of ≈ 0.2 eV at the surface between the blue and magenta curve. The corresponding dipoles in the vdW gaps for z < -20 Å still lead to a noticeable effect in the potential, i.e., to the difference between the yellow and black line in Fig. 5, although the variations in $\Delta \rho(z)$ are already very small in this region. The role of the vdW gaps is investigated in detail in the next section.

B. Role of the van der Waals gaps

The observations described in the previous section give rise to the question concerning the origin of the charge density oscillations. As the slope of the Coulomb potential is steeper in the vdW gaps than in the QLs, one might wonder whether the band bending is a general effect for crystals with a layered structure, where contiguous layers of some material are only weakly bound to each other. To investigate this question, we construct two model crystals: Artificial BiSe and "van der Waals silicon" (vdW-Si).

The artificial BiSe crystal has basically the same structure as Bi_2Se_3 , but it is built up of alternating bismuth and selenium layers instead of the quintuple layers. While in Bi_2Se_3 , there are three different interatomic distances in the unit cell, the artificial BiSe has only one interatomic distance for which we use the distance between the outermost Se atom of a QL and the adjacent Bi atom. This artificial crystal incorporates a chemical binding very similar to the binding in Bi_2Se_3 , but it does not have the layered QL structure. We use a slab with 55 atomic layers, corresponding to a thickness of ≈ 85 Å. The slab is terminated by Se on both sides. While Bi_2Se_3 is a semiconductor, BiSe is a metal.

The vdW-Si crystal is built of stacked Si(001)-(1 \times 1) slabs with the surface atoms of each slab being saturated with hydrogen atoms in order to ensure a weak interaction between two contiguous slabs. We show results for slabs consisting of six Si layers and a distance of 2.5 Å between two slabs. We use a crystal with five such Si slabs and a symmetric setup with potassium adsorbed in on-top position with a distance of 3.2 Å on both sides of the crystal [51]. Calculations with slabs of four Si layers in a slab or smaller distances between the slabs yield similar results.

Figure 7 shows $\Delta\rho(z)$ and the corresponding Coulomb potential of K-covered BiSe. At first glance, the behavior of $\Delta\rho(z)$ in BiSe is very similar to the behavior in Bi₂Se₃ (Fig. 5): They are identical close to the surface. Farther inside the crystal, $\Delta\rho(z)$ shows oscillations with comparable amplitudes in both materials. Nevertheless, the resulting Coulomb potentials are strikingly different: Instead of a long-ranged behavior, the potential of BiSe shows a steep increase from the surface towards the substrate for z > -5 Å with only little variations



FIG. 7. (Color online) The same picture as Fig. 5, but for K-covered artificial BiSe instead of Bi₂Se₃.

for z < -5 Å (see lower part of Fig. 7). The reason for the differing potentials lies in the details of $\Delta \rho(z)$.

A simple model consideration explains why the potentials of Bi₂Se₃ and BiSe show drastic differences, although at first glance the charge densities from Figs. 5 and 7 seem to be quite similar. To model this behavior, we consider a one-dimensional charge density $\rho(z)$ in a certain interval $I = [0 : z_I]$. We assume the charge density to be zero outside of I and only consider charge neutral systems, i.e., we have a total charge Q of

$$Q = \int_{-\infty}^{\infty} \rho(z) dz = \int_{0}^{z_{I}} \rho(z) dz \stackrel{!}{=} 0.$$
 (12)

From $\rho(z) = 0$ outside *I*, the Poisson equation $\partial_z^2 V(z) = -\rho(z)$ directly yields V = const outside *I*. If $\rho(z)$ is periodic in *I* with *n* periods [e.g., $\rho(z) = A \sin(2\pi nz/I)$], it consists of *n* identical consecutive dipoles. The Coulomb potential of one isolated dipole of these *n* dipoles has a potential difference V_1 between the (constant) potentials on the left and right side of the dipole. The size of the potential step V_1 and the course of the potential in the region of the dipole depend on the details of $\rho(z)$. The potential of $\rho(z)$ (the *n* dipoles) will have a difference $V(\infty) - V(-\infty) = V(z_I) - V(0) = n \cdot V_1$. The size of V_1 depends on the amount of charge *Q* that forms the dipole and the spatial distance *d* between the two charges +Q and -Q. In the case of a simple plate capacitor, $V_1 \propto Qd$ holds.

The structure of $\Delta \rho(z)$ in Bi₂Se₃ is similar to this model. We have an approximately periodic charge density in a limited space area, i.e., in the crystal [see Fig. 6: The decay-corrected charge density difference has (nearly) the same structure on every QL (marked by dotted vertical lines)]. But there is still an important difference to the simple model explained above: The dipoles do not all have the same amplitude, but the



FIG. 8. $\Delta \rho(z)$ and $V_{\text{coul}}(z)$ for K-covered van der Waals silicon (see text for explanation).

amplitude gets smaller deeper in the crystal, i.e., the charge Q inside the dipoles is reduced. So the dipoles farther away from the surface cause smaller potential steps than the dipoles close to the surface. These two properties (a periodic structure combined with a decaying amplitude) of the observed charge density difference in Bi₂Se₃ lead to the long-ranged potential.

The behavior of artificial BiSe can also be revealed within this model. Here, $\Delta \rho(z)$ exhibits no periodic structure. Therefore there are no repeated, periodic dipoles whose potential steps add up, but there can be dipoles of opposite orientation that neutralize each other or even lead to a negative potential step. This can be seen in Fig. 7: For z < -5 Å, the potential shows an oscillating behavior rather than a monotonic increase. In this case, the irregular variations in $\Delta \rho(z)$ even lead to a slight upward band bending for z < -5 Å while a quite short-ranged downward bending occurs for z > -5 Å.

All these issues confirm that the layered structure of Bi_2Se_3 is crucial for the band bending which can be explained by regular oscillations in $\Delta \rho(z)$ that do not occur for artificial BiSe. Nevertheless, the layered structure of Bi_2Se_3 is not the only reason for the band bending in this material, as can be seen from comparison with vdW-Si.

Figure 8 shows $\Delta \rho(z)$ and $V_{\text{coul}}(z)$ for K-covered vdW-Si. In this case, $\Delta \rho(z)$ is only nonzero close to the surface, despite the layered structure of the crystal. Accordingly, we do not observe the formation of a long-ranged potential; $V_{\text{coul}}(z)$ is only nonzero on the first Si slab, and even here the maximal value is small with $|V_{\text{coul}}| \approx 0.11$ eV. This means that band bending is *not* a general effect for layered crystals in the sense that any layered structure *inevitably* leads to band bending. Both the involved chemical species and the presence of vdW gaps are important for the question whether a long-ranged potential appears or not. The sheer existence of vdW gaps in a crystal is therefore not sufficient for the occurrence of band bending.

We infer that Si is very robust against variations of the charge density deeper in the crystal. A rearrangement of charges at the surface (e.g., caused by the adsorption of atoms) can be screened on a short length scale (a few angstroms), presumably due to surface states resulting from dangling bonds which take up most of the transferred charge. The introduction of vdW gaps in the crystal does not change this

-40 - 30 - 20 - 10

z [Å]



FIG. 9. $\Delta \rho(z)$ and $V_{\text{diff}}(z)$ for K-covered Bi₂Se₃ with reduced (left) and increased (right) vdW gap d_{vdW} . The real crystal has $d_{\text{vdW}} = 2.43$ Å. The gray areas indicate the vdW gaps.

0

-40 - 30

-20 -10 0

z [Å]

behavior, therefore no band bending is observed in vdW-Si. In contrast, Bi and Se atoms as arranged in BiSe or Bi₂Se₃, respectively, are very susceptible to changes in the charge density. There are no surface states resulting from dangling bonds, therefore the states affected by adatoms are bulklike. The vdW gaps introduce a periodicity in the crystal which leads to a corresponding periodicity in $\Delta \rho(z)$ and eventually results in a long-ranged (Coulomb) potential. We observe very similar band bending effects in calculations for the related compounds Bi₂Te₃, Sb₂Te₃, Bi₂Te₂Se, and Bi₂Se₂Te.

It is also interesting to investigate the influence of the spatial width d_{vdW} of the vdW gap. In addition to the calculations discussed so far, which were done for Bi₂Se₃ in its natural structure ($d_{vdW} = 2.43$ Å), we also calculate $\Delta \rho$ and V_{diff} for Bi₂Se₃ with a vdW gap reduced by 0.5 Å ($d_{vdW} = 1.93$ Å) and increased by 1 Å ($d_{vdW} = 3.43$ Å), respectively. The results displayed in Fig. 9 show that the main effect of the vdW gaps is the formation of dipoles in the vdW gaps. Charge is shifted from one edge of the vdW gaps to the other. As the vdW gaps increase, their role becomes more important: For large vdW gaps, the dipoles in the vdW gaps and flat on a QL. For small vdW gaps, the charge density variation in the vdW gap is not significantly stronger than inside a QL and thus the vdW gaps are less prominently seen in both $\Delta \rho(z)$ and $V_{diff}(z)$.

We emphasize that the screening in Bi₂Se₃ is in a sense counterintuitive. Regarding the relatively large dielectric constant $\epsilon_{\infty} \approx 25$ of Bi₂Se₃ [52], one might expect the crystal to be more "metallic" than silicon ($\epsilon_{\infty} = 12$) [53] in the sense that perturbations of the charge density can be screened on very short length scales. Accordingly one would expect $\Delta \rho \neq 0$ only close to the surface in Bi₂Se₃. However, this is not the case. In fact, artificial BiSe is a metal and shows $\Delta \rho \neq 0$ deep inside the crystal (see Fig. 7), whereas Si is a semiconductor and exhibits the opposite behavior. The pure value of ϵ_{∞} is not a helpful number for the explanation of the band bending, because it is an averaged quantity for a macroscopic crystal.

V. BAND BENDING WITHOUT ADATOMS: SELENIUM VACANCIES

The results obtained in this work as well as in the other studies mentioned above suggest that the band bending effects are related to the properties of Bi_2Se_3 . Therefore they should occur for all perturbations that induce a distinct charge rearrangement at the surface, such as other types of adsorbates or vacancies. For instance, we have investigated the adsorption of atomic hydrogen on the Bi_2Se_3 surface and find the same kind of band bending effects. As a further example with similar results, we now discuss briefly the effect of selenium vacancies in the surface layer and compare it with the effect of K adsorption.

Studying vacancies offers a major advantage over calculations with other kinds of adsorbates, since this provides an undisturbed insight into the band bending process due to the absence of adsorbate-specific influences. The electronic properties of Bi₂Se₃ with Se vacancies in the surface layer have formerly been investigated by Yan *et al.* [21], but they have not discussed their results with respect to band bending. In our calculations, we use a $\sqrt{3} \times \sqrt{3}$ unit cell in which we remove one of the three Se atoms in the surface layer. We find that $\Delta \rho(z)$ and $V_{\text{diff}}(z)$ show a similar behavior as in the case of K adsorption. An experimental study discussing Se vacancies as possible origin of the band bending can be found in Ref. [12].

The band structure is plotted in Fig. 10. The comparison with the 1/3 ML K-coverage band structure (cf. Fig. 2) is most straightforward. Overall, there are many similarities in the electronic structure. For the surface with a Se vacancy,



FIG. 10. (Color online) The band structure of Bi_2Se_3 with selenium vacancies in the surface layer. The blue and red dots mark the spin expectation value as in Fig. 2.

the Dirac point is shifted to lower energies (compared to the pristine surface) and cannot be identified any more. Below the CBM at $\overline{\Gamma}$, Rashba-like states have emerged. These two features are a strong indication for band bending. The potassium state at 0.65 eV from Fig. 2 is now absent, of course. Instead, at this energy we observe a spin-polarized surface state which is evoked by the vacancy and shows a completely different dispersion. There is also a state that emerges from the upper edge of the pocket around $\overline{\Gamma}$.

These similarities and our analysis of the charge densities and potentials (which is not shown here) show that a band bending effect can not only be induced by adatoms on the Bi_2Se_3 surface, but also by Se vacancies in the surface layer. This shows that the band bending mechanism can not only be activated by external charges (from adatoms) that are transferred to the crystal. The formation of vacancies in the surface leads to a similar rearrangement of charges close to the surface as K adsorption. Accordingly, the reaction of the charges deeper in the crystal is the same: Dipoles are built, as discussed in the previous section, and eventually the band bending emerges. The results for vacancies further confirm that the band bending is a property of Bi_2Se_3 itself and not of a specific adatom on the surface.

VI. SUMMARY

We have employed density-functional theory to investigate adatom- and vacancy-induced band bending at the surface of the topological insulator Bi₂Se₃. The adsorption of K adatoms gives rise to significant changes in the band structure of a pristine Bi₂Se₃ surface. Some of the new bands are specific to potassium while most of the adsorption-induced states result from a long-ranged potential inside the crystal and are of more general nature, therefore. Rashba-like states below the conduction band minimum, \mathcal{M} -shaped states in the valence band pocket around $\bar{\Gamma}$, as well as \mathcal{W} -shaped bands in the first conduction band pocket belong to the class of bands resulting from band bending. We observe similar states for Se vacancies in the topmost surface layer.

The long-ranged potential, which is responsible for the occurrence of the states mentioned above, is observed in

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calculations both with and without SOC included, therefore it is not related to the topological character of Bi_2Se_3 . The potential occurs for K adsorption as well as in the case of Se vacancies. We identify the following ingredients needed for the formation of the long-ranged potential in Bi_2Se_3 :

(1) A distinct perturbation of the surface. The creation of a surface by cleaving of bulk Bi₂Se₃ between two quintuple layers gives rise to gap-closing surface states due to the topological nature of the crystal. However, this perturbation of the bulk is weak in the sense that no substantial charge rearrangement occurs since the inter-QL bonding is weak. As a result, no significant band bending occurs for a clean surface of undoped Bi₂Se₃. Instead, defects or adsorbates are necessary for band bending.

(2) The possibility to evoke variations of the charge density far away from the surface. In contrast to the presented case of silicon, the chemical and structural composition of bismuth selenide (both with and without vdW gaps) enable such changes in the charge density.

(3) The layered structure of the material. The vdW gaps of Bi_2Se_3 give rise to a periodic rearrangement of the charges inside the crystal. Accumulation and depletion of the charge at the two boundaries of each quintuple layer, respectively, lead to dipole potentials like those of consecutive plate capacitors. The resulting electrostatic potential shows characteristic steps in the van der Waals gaps of Bi_2Se_3 . It decays with increasing distance from the surface since the adsorbate-or vacancy-induced charge rearrangement is damped in the crystal.

The question whether or not band bending occurs as a universal effect in layered "van der Waals materials" might also be relevant for other material classes, e.g., the large family of transition metal dichalcogenides [54,55].

For all investigated perturbations at the surface of the TI Bi_2Se_3 , we find the often-cited robustness of the surfaces states remaining in the sense that the fundamental bulk band gap is closed by states which are localized at the surface. Nevertheless, the spin properties of these states, as well as the positions of possible Dirac points distinctly depend on the actual bonding configuration at the surface.

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