Topological insulators (TIs), characterized by a non-trivial insulating gap in the bulk and topologically protected helical states on the boundaries, are a new frontier in condensed matter physics and materials science [1, 2]. Topological surface states (TSSs) in three-dimensional (3D) TIs, such as the Bi$_2$Se$_3$ family with a single Dirac cone, have attracted particular attention [3]. While the TSSs are robust against time-reversal-invariant perturbations, the breaking of time-reversal symmetry (TRS) opens up an energy gap at the Dirac point. One way to explore the response of the TSSs to TRS breaking is via magnetic ordering. Apart from being a prerequisite for future spintronic applications, the presence of magnetic order in 3D TIs can manifest itself in novel quantum phenomena, such as the Quantum Anomalous Hall effect [4, 5] and the topological magnetoelectric effect [6].

For the important case of magnetic acceptors, e.g. Mn on (111) Bi$_2$Se$_3$ surface, a detailed microscopic description, consistent with experimental observations, is lacking. There is a strong experimental evidence that Mn behaves as a substitutional acceptor in the Bi$_2$Se$_3$ family of 3D TIs [10–15]. Typically, Mn substitutes Bi in Bi$_2$Se$_3$ in the ($d^5$) configuration, corresponding to the +2 valence state, giving rise to a spin $S = 5/2$. Since the nominal valence of Bi is +3, this implies that substitutional Mn impurities also introduce acceptor (hole) states in the bulk gap of the host material, similarly to Mn in GaAs, a typical DMS. These acceptor levels can be directly probed by STM experiments [16]. However, the nature of these states and their interplay with the Dirac surface states have not yet been analyzed theoretically.

In this Letter we investigate single substitutional Mn impurities on the (111) surface of Bi$_2$Se$_3$, using density functional theory (DFT) and tight-binding (TB) models. We find that Mn$^{2+}$ introduces a mid-gap acceptor state, localized mainly on the impurity and the nearest-neighbor (NN) Se atoms, similar to a substitutional Mn in GaAs [19]. Our calculations demonstrate the importance of electronic correlations at the impurity site, which we model by a Hubbard $U$ parameter [20]. The $U$ parameter controls the position of the impurity $d$-orbitals, which in turns determines the hybridization with the $p$-orbitals of NN Se atoms and the acceptor spin-polarization. Increasing $U$ localizes the Mn $d$-states, leading to an enhancement in the Mn magnetic moment and a weakening of the $p$-$d$ hybridization and the acceptor polarization. With the Mn placed on one of the surfaces of a finite slab, the spin-polarized acceptor states couple quasi-resonantly with the helical TSS at the same surface, opening a gap of a few meV at the Dirac point. The magnitude of the gap is significantly affected by the strength of the $p$-$d$ hybridization. With the appearance of the energy gap, the system exhibits a finite magnetization, with out-of-plane polarization direction [7, 8].
The DFT calculations were performed using the full-potential all-electron method with the basis consisting of linearized augmented plane waves combined with local orbitals (LAPW+lo), as implemented in the WIEN2k package. We use the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. We consider a $2 \times 2$ surface supercell containing six quintuple layers (QLs) of Bi$_2$Se$_3$. A Bi atom in the second monolayer (ML) below the surface is replaced by a Mn atom (Mn doping of 2%). The direction of the magnetization expressed in terms of lattice vectors is along [001] (z-axis), which is perpendicular to the (111) surface. A vacuum of 30 Bohr is added along the [001] direction to avoid supercell interaction. The atomic positions in the supercell have been fully relaxed. We use four non-equivalent k-points in the Brillouin zone including the Γ point for charge- and energy-convergence. We account for electronic correlations at the impurity site by means of the (GGA+$U$)-method. Below we consider explicitly the two cases $U = 0$ and $U = 4$ eV.

We start with the DFT band structure of a pristine Bi$_2$Se$_3$ slab, plotted in Figs. (a)-(b), showing the expected conical TSS crossing at the Dirac point. In fact, the TSS consists of two degenerate states, one for each slab surface [see panels (a) and (b)]. For the particular slab considered, these state are only slightly coupled, introducing a very small ($\lesssim 1$ meV) gap at the Dirac point. The DFT bandstructure of Mn dopants substituted on one (the TOP) of the slab surfaces is plotted in Fig. (c), for the case $U = 0$. It is characterized by the following features: (i) the conical TSS belonging to the top surface (where the impurity resides) has been pushed up in energy. The bottom TSS is essentially unaffected by the impurity [see also Figs. (c)-(f), where top and bottom states are highlighted]; (ii) the two displaced conical TSSs exhibit avoided level crossings, with a gap of the order of 20 meV, at two symmetric k-points with respect to the Γ point; (iii) the Dirac point of the top (bottom) TSS is now above (below) the Fermi energy ($E = 0$). For the top TSS there is an energy gap of approximately 5.5 meV at the Dirac (Γ) point [see the inset in Fig. (c)]. As we explain below, this gap is caused by TRS breaking due to magnetic doping. For the bottom TSS the gap remains negligible, i.e. $\sim 1$ meV, as in the pristine case; (iv) the states in the energy window $E \in [0,0.13]$ eV, not belonging to the bottom TSS, result from the complex hybridization of Mn d–levels, NN Se p–levels and the extended top TSS [see Figs. (d)-(f)].

In order to explain some of these features, we now consider a $sp^3$ tight-binding (TB) model for Bi$_2$Se$_3$, with parameters fitted to DFT calculations. The TB model incorporates intra-atomic spin–orbit coupling and takes into account hopping between second-nearest-neighbor MLs. An impurity is introduced in the TB model via a modification of the local on-site potential (spin-dependent in the case of a magnetic impurity). Figures (a)-(b) shows the bandstructure of a 6QL-thick slab of Bi$_2$Se$_3$ calculated with the TB model, where a non-magnetic or a magnetic impurity is substituting Bi in the second ML below the (111) surface. In the non-magnetic case, as a result of asymmetric doping, one of the two degenerate (for pristine Bi$_2$Se$_3$) Dirac cones, corresponding to the doped surface, is shifted up in energy. The TSS of the un-doped surface remain nearly unaffected, which is expected for a relatively thick slab. Since the TRS is preserved, the states corresponding to the two shifted Dirac cones at Γ have two-fold degeneracy related...
to the opposite spins [see upper inset in Fig. 2(a)]. However, the asymmetric doping breaks the inversion symmetry (IS), therefore away from Γ the degeneracy is lifted and avoided crossings are formed at two symmetric positions in the Brillouin zone, producing a gap, which can be seen in the lower inset of Fig. 2(a) (this gap should vanish in the limit of an infinitely thick slab). The presence of the magnetization breaks the TRS, which leads to the lifting of the degeneracy at all k-points. Indeed, in the magnetic case, in addition to the features related to asymmetric doping, we find a sizable gap at the Γ point for the Dirac cone of the doped surface [see the upper inset of Fig. 2(b)].

We now focus on the properties of the unoccupied electronic states, which appear above the Fermi level in our DFT bandstructure calculations (Fig. 1). There are three elements contributing to these states, (i) the impurity levels (Mn d–orbitals), (ii) the Mn-acceptor states, and (iii) the TSSs. Figure 3 shows the spin-resolved density of states (DOS) around the Fermi energy for the d–orbitals of Se atoms on the top and bottom surfaces, as well as for the Mn d–orbitals, for two different choices of U (U=0 and U=4 eV).

The calculated magnetic moment of the Mn atom on the surface (with SOI) is 4.67 µB for U=4 eV, indicating that a substitutional Mn is close to its +2 valence state. Given the nominal +3 valence state of Bi in Bi₂Se₃, we conclude that the substitution of a Bi with a Mn introduces an acceptor (hole) state. Its wave function is localized primarily on the surroundings of the dopant and, to a lesser degree, on the dopant itself. For U=0 some of the Mn d–orbitals appear close to the Fermi level [Fig. 3(c)], in the same energy range as the Se p–orbitals, leading to their hybridization. Importantly, the top surface Se p–states around the Fermi level are visibly spin-polarized [Fig. 3(a)]. The d–hybridized Se p–orbitals above the Fermi level close to the Mn are the main contributors to the Mn-acceptor (hole) states. With increasing U, the majority Mn d–orbitals are pushed deeper into the valence band [Fig. 3(f)], decreasing the hybridization with Se p–orbitals on the top surface, where the impurity is located. The Mn magnetic moment increases by ~7% with respect to the U = 0 value. The decrease of the spin-polarization with increasing U [Fig. 3(d)] further confirms the dependence of the hybridization on the relative position of the Mn d– and Se p–orbitals.

The appearance of these unoccupied states above the Fermi level, spatially localized around the Mn, is an indication of the acceptor level. As shown in Fig. 3(d), these states occur in the same energy range E ∈ [0, 0.13] eV of the TSS of the top surface, and energetically are not far from its Dirac point. This is crucial for the opening of the gap. In contrast, in the range E ∈ [0, 0.13] eV the bottom surface states [Fig. 3(b), (e)] are essentially the TSS, with negligible coupling the impurity wavefunction. Their linear dispersion is preserved and still detectable in the bandstructure in Fig. 1(e).

To clarify the nature of the Mn-acceptor independently of the TSS, we perform calculations without SOI, which greatly simplifies the electronic structure around the Fermi energy. Figure 3(a) shows a few atomic layers of Bi₂Se₃ near the (111) surface, with a Bi substituted by Mn atom in the second ML. There are eight Se atoms surrounding the Mn, four above and four below. Two Se atoms, indicated by the red arrows, are further apart from the Mn compared to the other six Se atoms.
which are NN to the Mn. In Figs. 4(b)-(e) we present the total DOS and the partial DOS for the Mn impurity and surrounding Se atoms, calculated without SOI. We conclude that the peak in the total DOS (mainly majority spin) right below the Fermi level, is predominantly due to the Mn $d$-levels and the NN Se $p$-levels, with a very small (but finite) contribution from other Se atoms around the Mn. The highly spin-polarized character of the $p$-states around the Fermi level is a consequence of the hybridization between the Mn $d$-orbitals and the NN Se $p$-orbitals. Our calculations with $U=4$ eV (not shown here) confirm this observation. Similar to the calculation with SOI (see Fig. 3), we find that for $U=4$ eV, the Mn $d$-orbitals are more localized and are pushed deeper into the valence band, which reduces the $p$-$d$ hybridization and decreases the polarization of NN Se $p$-states by a factor of two.

We now examine the spatial character of the Mn acceptor state, which is directly accessible by STM experiments. Figures 5(b)-(e) show simulated STM topographies for a Mn in the vicinity of the (111) Bi$_2$Se$_3$ surface. These images are obtained by plotting the electronic local density of states (LDOS) around the Mn, integrated in the energy window $[0, 0.13]$ eV (empty states) and $[-0.13, 0]$ eV (filled states) around the Fermi level (calculations are done with $U=0$). Panels (d), (e) represent LDOS at the (111) surface, while panels (b), (c) show LDOS at 1 Å above the surface. Figures 5(c) and (e) clearly show that the acceptor state is predominately localized around the Mn and its three NN Se atoms. The state is composed of three $p$-like Se orbitals pointing to the Mn in the middle, visibly deformed by the hybridization. The state exhibits characteristic triangular shape similar to the experimental STM topography observed at positive bias in Mn-doped Bi$_2$Te$_3$ [16]. The LDOS for filled states below the Fermi level [see Figs. 5(b) and (d)] are much less affected by the presence of the impurity.

In Fig. 5(a) we plot a side view of the empty-state LDOS along the slab, projected in the $xz$-plane. The figure confirms that the states in the energy range $[0, 0.13]$ eV are predominantly localized around Mn and its nearest neighbor Se atoms, which is a signature of the Mn-acceptor. However, these states also display their ex-
tended character within ~1 QL from the surface, which is a typical decay length of the TSS [24]. Clearly, the Mn-acceptor has a strong spatial overlap with the TSS of the top surface. Furthermore, as shown above, these two states are quasi-degenerate in the energy range [0, 0.13] eV, and therefore they couple strongly. It is precisely the quasi-resonant coupling of the spin-chiral TSS with the spin-polarized Mn acceptor that ultimately opens a gap at the Dirac point [see Fig. 1(c)]. Strong support for this spin-polarized Mn acceptor that ultimately opens a gap is provided by the observation that the gap decreases from 5.5 meV to 3.2 meV when $U$ increases from 0 to 4 eV. As we have seen, strong correlations at the impurity site decrease the Mn d– and Se p–orbital hybridization, leading to a smaller spin-polarization of the acceptor. Isolated spin-polarized Mn d-levels are further away both in energy and in space from the TSS at the Dirac point. Therefore their spin-dependent potential alone is less effective in inducing the TRS breaking necessary to open a gap.

In conclusion, our calculations show, in agreement with experiments [12][18], that substitutional Mn impurities on Bi$_2$Se$_3$ surface introduce spin-polarized acceptor states, whose properties are similar to Mn-acceptors in GaAs. We find that the mechanism for the opening of a gap at the Dirac point is provided by the spatial overlap and the quasi-resonant coupling between the Mn-acceptor and the topological surface states inside the bulk band gap of Bi$_2$Se$_3$. The signatures of this coupling can be detected in STM experiments, addressing specifically magnetic dopants on a 3D TI surface. The present study contributes to clarify the origin of surface-ferromagnetism in transition-metal-doped Bi-chalcogenide thin films. We should note that recent STM experiments in these systems suggest that, despite the similarities to DMSs, carrier-independent mechanisms might also be relevant for establishing the ferromagnetic state [22]. Further experimental and theoretical studies, addressing the role of bulk dopants and the position of the Fermi level in the bulk band gap, are necessary to elucidate this point.

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