Spin-texture and magnetic anisotropy of Co adsorbed Bi$_2$Se$_3$ topological insulator surfaces

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Based upon first-principles methods, we investigate the magnetic anisotropy and the spin-texture of Co adatoms embedded in the topmost Se network of the topological insulator Bi$_2$Se$_3$ surface. We find that the formation of energetically stable magnetic moment perpendicular to the surface plane, $S_z$, of Co adatoms on the TI Bi$_2$Se$_3$ surface indicates the presence of helical spin-texture not only in the massless surface Dirac states, but also surface states resonant within the valence band present spin-texture. On the other hand, upon the presence of Co adatoms we find that the out-of-plane surface magnetism represents the dominant spin state ($S_z$), while the planar spin components, $S_x$ and $S_y$, are almost suppressed.

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Topological insulators (TIs) compose a new quantum matter phase in solid state physics that may provide an emplacement for fundamental physics understanding as well bases for novel technologies, such as topological quantum computing, information processing and spintronic applications. Recently 3D TIs were predicted by Fu et al. $^1$ and experimentally observed by Hsieh et al. $^2$ in Bi$_{1-x}$Sb$_x$. Further, other compounds like Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Te$_3$, and TIBiSe$_2$ were identified as 3D TIs. $^3$$^4$$^5$$^6$ In these materials the spin-orbit (SO) interaction rules the formation of topological states. While the bulk is insulating, on the edges there are robust conducting states. Indeed, on the surface they present a (single) Dirac crossing at the $\Gamma$ point. They show a spin-texture that allows spin currents without dissipation, supressing back-scattering if time reversal symmetry (TRS) is preserved. In this way the understanding of how the protected surface states behaves in the presence of impurities is an important subject to be explored, especially for technological applications. Magnetic impurities can destroy the robust surface metallicity by breaking TRS, while nonmagnetic impurities maintain TRS. The interaction between a magnetic moment and the topologically nontrivial surface states opens a surface band gap. $^6$$^7$$^8$$^9$ In this context an important issue to be investigated is the energetic stability of the spin orientation, and the changes on the spin-texture upon the adsorption of transition metal on TI surfaces, which is especially desired for spintronic and information processing applications.

In this letter, through the calculation of magnetic anisotropy energy (MAE) we find that Co adatoms lying on the TI Bi$_2$Se$_3$ surface exhibit energetically stable magnetic moment perpendicular to the surface. Further, spin-texture calculations reveal that the Co adatom exhibits spin component $\sim$100% polarized out-of-plane, whereas the helical spin-texture of the massive Dirac cone is drastically reduced. In addition, in consonance with previous experimental findings, the presence of Co adatoms breaks TRS, opening up a surface band gap, giving rise to massive Dirac fermions.

Our results were obtained performing ab-initio electronic structure calculations, using the density functional theory (DFT) within the generalized gradient approximation (GGA) for the exchange and correlation potential. $^{12}$ The SO interaction have been self-consistently treated by using fully relativistic pseudopotential within the projector augmented wave method (PAW). $^{12}$ We use the Vienna Ab initio Package Simulation (VASP). $^{14}$ A plane wave basis set is used, with a cut-off energy of 300 eV. The Brillouin-zone is sampled, according to the Monkhorst-Pack scheme, by using a number of k-points such that the total energy is converged. The (111) surface of Bi$_2$Se$_3$ was investigated using slab method with a vacuum layer of at least 8Å. Here we have used a thickness of 4 quintuple layers, keeping the experimental lattice parameter. We verify that this slab is enough to obtain the correct surface massless Dirac cone.

In Fig. 1 we show the band structure around the bulk band gap, and the surface spin-texture when a Co atom is adsorbed onto Bi$_2$Se$_3$ surface. The surface spin-texture is affected by the presence of the magnetic impurity, as we can see in Fig. 1-b–j. The original massless Dirac cone (black dotted lines) is now splitted (purple line) where the lower massive Dirac cone lies below the bulk valence band, and the upper massive Dirac cone stays inside the bulk band gap, Fig. 1a. Thus, indicating that the TRS has been removed upon the presence of Co adatoms on the TI surface.

The calculated expectation values of $S_x$ and $S_y$ of the surface protected massless Dirac cone for the pristine
Bi$_2$Se$_3$ (black lines of Fig. 1) are $\sim$60% spin-polarized with respect to $\hbar/2$, in agreement with a recent calculation. By looking at Figs. 1e and 1f we see that the $S_x$ and $S_y$ for the electronic states of the upper massive Dirac cone far from the $\Gamma$ point of the Brillouin zone, are somewhat the same as compared to the ones of pristine Bi$_2$Se$_3$ surface. On the other hand, for wave vectors near the $\Gamma$ point, $k \to \Gamma$, those spin components tend to zero. That is, the projection of the spin-components on the $xy$ plane becomes negligible. Meanwhile, as depicted in Fig. 1g, there is an increasing on the out of the plane, $S_z$, component close to the center of the Brillouin zone, which can be attributed to the formation of Co-Se chemical bonds. Here the expectation values of spin components are obtained from $\langle S_\alpha(\vec{k}) \rangle = \hbar/2\langle \Psi(\vec{k})|\sigma_\alpha|\Psi(\vec{k}) \rangle$, where $\Psi(\vec{k})$ is the spinor wavefunction and $\sigma_\alpha$ are the Pauli matrices. These results are in agreement with recent theoretical calculations based on few band phenomenological models. 

We find (five) $d$ orbitals inside the bulk band gap mostly localized in the Co atom (Fig. 1a). We can separate these orbitals in two classes according to their symmetry. Two of them (red and pink lines) suffer a strong hybridization with the surface Se atoms, resulting in a quasi-Dirac crossing at the $\Gamma$ point. These two orbitals have Se-$p_z$ and Co-$d_{xy}$ and $d_{x^2-y^2}$ symmetry characters. As we can see from Fig. 1h and 1i they present small $S_x$ and $S_y$ spin components, and the left-handed spin helicity has been maintained, while there is an out of plane $S_z$ of around $\hbar/4$ for the electronic states near the edge of the Brillouin zone, Fig. 1j). The other three Co-3$d$ orbitals (green lines of the Fig. 1a) are more localized, being two occupied bands ($d_{xy}$, $d_{x^2-y^2}$) and one unoccupied ($d_z$). The magnitude of the $S_z$ component of these three bands is $\sim \hbar/2$ spin aligned perpendicular to the TI surface (see Fig. 1d), and do not depend on $k$-direction. In contrast the Co-$d_{xy}$ and $d_{x^2-y^2}$ (Fig. 1j), due to the hybridization, the spin polarization is dependent on the $k$-direction.

It is worth to point out that the results presented in Fig. 1 are for a Co coverage of 1/9 monolayer (ML). In addition we have considered coverages of 1, 1/4 and 1/16 ML, as schematically depicted in Fig. 2 For 1/9 ML Co coverage on the surface of Bi$_2$Se$_3$ there is not new Dirac point, but two bands (red and pink lines of this figure) are getting close at the $\Gamma$ point. By increasing the Co coverage to 1 or 1/4 ML, this two bands are split. However by decreasing the Co coverage to 1/16 ML the two bands touch each other at the $\Gamma$ point, forming a new Dirac cone, similarly as experimentally observed for Fe deposited on Bi$_2$Se$_3$. We verify that the spin-texture for the other bands (then the red and pink ones from Fig. 1) are similar for all Co coverages.

In order to understand the spin projection as a function of the energy states we plot in Fig. 3 the Spin-Density projected for each spin component ($\alpha = x, y, z$). This projection was computed for a mesh of $k$-points along the $K_x$-$\Gamma$-$M_y$ direction. For pristine Bi$_2$Se$_3$ (Fig. 2 b and -c) we observe that the occupied massless Dirac cone presents higher density of spins than the unoccupied one. From this figure we also observe that there is a spin-texture for states inside the bulk valence band reaching $\sim$1 eV below the Fermi level. These spin-textures are due to the presence of surface states resonant within the bulk valence band. When the Co atom is adsorbed on the TI surface (Fig. 3d and -e) the $\langle S_x \rangle$ and $\langle S_y \rangle$ components reduce drastically, while the $\langle S_z \rangle$ increases, showing that the out-of-plane surface magnetism are the dominant spin states.

The Co atom adsorbed on the Bi$_2$Se$_3$ surface is bonded to three top surface Se and three Bi atoms of the second layer, as showed inset of Fig. 2. This system is exothermic by 2.09 eV per Co atom with respect to clean surface and isolated Co dimers. There is an attractive interac-
FIG. 2: (Color online) Schematic representation of Co adsorbed on the TI surface for 1, 1/4, 1/9 and 1/16 monolayer coverages, from (a) to (d), respectively. The whiter balls represent the Se topmost surface layer, and the red balls represent the embedded Co atoms.

FIG. 3: (Color online) Band structure (a) and Spin-Density projected on each $S_\sigma$ spin component for pristine Bi$_2$Se$_3$ along the $\Gamma$-K (b) and $\Gamma$-M (c) directions. (d–e) The Spin-Density projections for the system when a Co atom is adsorbed on the TI surface. The positive and negative signs for $<S_\sigma>$ are with respect to the $K_x$–$\Gamma$–$M_y$ directions, as indicated inset at the hexagon diagram. The left-handed helicity shown in the hexagon diagram is for a cut above the Fermi level.

FIG. 4: (Color online) Adsorption energy as a function of Co-Co average distance distributed on the surface of Bi$_2$Se$_3$. The adsorption energy is computed with respect to the clean surface and isolated Co$_2$ dimer. Inset is the atomic arrangement when a Co atom is adsorbed on the Bi$_2$Se$_3$ surface. The Co atom is bonded to the first (Se) and second (Bi) atomic layers.

FIG. 5: Magnetic anisotropy energy computed as the total energy as a function of the magnetic moment alignment. The zero angle is for a magnetic moment aligned out-of-plane, perpendicular to the TI surface (z direction). xy is the basal TI plane.

In summary our first principles calculations provide a fundamental understanding of TI properties upon the adsorption of a magnetic impurity. The adsorbed transition metal Co impurity, give rise to massive Dirac fermions, can works as a local magnetic field inducing an anomalous Hall effect. [18, 21]

The spin-texture of the TI–magnetic-impurity system is dependent on the spin polarization. In order to verify the energetic stability of our calculated spin-texture (Fig. 1 and 3) we calculate the magnetic anisotropy energy of the magnetization induced by the Co adatoms on the Bi$_2$Se$_3$ surface. As we can see in Fig. 5 the minimum energy occurs for the magnetic moment aligned perpendicular to the TI surface, and the energy barrier is verified when the magnetic moment is in-plane. A single Co impurity adsorbed on TI surface presents a MAE of 6 meV per impurity.
inducing an energetically stable out-of-plane spin component, $S_z$, ruled by the Co 3d electronic states lying within the bulk band gap. This $S_z$ component is $\sim100\%$ polarized, whereas the polarization of the surface helical spin-texture of the massive Dirac cone is drastically reduced with respect to pristine Bi$_2$Se$_3$. The impurity introduces a net spin with MAE of 6 meV per adsorbed Co atom, favoring the magnetic moment to be aligned perpendicular to the TI surface. These results have a direct connection with information processing and spintronic applications using topological devices.

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[1] L. Fu, C. L. Kane, and E. J. Mele, Phys. Rev. Lett. 98, 106803 (2007).
[2] D. Hsieh, D. Qian, L. Wray, Y. Xia, Y. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) 452, 970 (2008).
[3] D. Hsieh, Y. Xia, L. Wray, D. Qian, A. Pal, J. H. Dil, J. Osterwalder, F. Meier, G. Bihlmayer, C. L. Kane, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Science, 323, 919 (2009).
[4] D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, N. P. Ong, A. V. Fedorov, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature (London) 460, 1101 (2009).
[5] Y. Xia, D. Qian, D. Hsieh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Phys. 5, 398 (2009).
[6] H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Phys. 5, 438 (2009).
[7] Y. L. Chen, J. G. Analytis, J.-H. Chu, Z. K. Liu, S.-K. Mo, X. L. Qi, H. J. Zhang, D. H. Lu, X. Dai, Z. Fang, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z.-X. Shen, Science 10, 178 (2009).
[8] T. Sato, K. Segawa, H. Guo, K. Sugawara, S. Souma, T. Takahashi, and Y. Ando, Phys. Rev. Lett. 105, 136802 (2010).
[9] K. Kuroda, M. Ye, A. Kimura, S. V. Eremeev, E. E. Krasovskii, E. V. Chulkov, Y. Ueda, K. Miyamoto, T. Okuda, K. Shimada, H. Namatame, and M. Taniguchi, Phys. Rev. Lett. 105, 146801 (2010).
[10] Y. L. Chen, H.-H. Chu, J. G. Analytis, Z. K. Liu, K. Igarashi, H.-H. Kuo, X. L. Qi, S. K. Mo, R. G. Moore, D. H. Lu, M. Hashimoto, T. Sasagawa, S. C. Zhang, I. R. Fisher, Z. Hussain, and Z. X. Shen, Science 329, 659 (2010).
[11] L. A. Wray, S.-Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, and M. Z. Hasan, Nature Phys. 7, 32 (2011).
[12] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[13] P.E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[14] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[15] H.J. Monkhorst and J.D. Pack, Phys. Rev. B 13, 5188 (1976).
[16] O. V Yazyev, J. E. Moore, and S. G. Louie, Phys. Rev. Lett. 105, 266806 (2010).
[17] Q. Liu, C.-X. Liu, C. Xu, X.-L. Qi, and S.-C. Zhang, Phys. Rev. Lett. 102, 156603 (2009).
[18] J.-J. Zhu, D.-X. Yao, S.-C. Zhang, and K. Chang, Phys. Rev. Lett. 106, 097201 (2011).
[19] D. A. Abanin, and D. A. Pesin, Phys. Rev. Lett. 106, 136802 (2011).
[20] L. A. Wray, S.-Y. Xu, Y. Xia, D. Hsieh, A. V. Fedorov, Y. S. Hor, R. J. Cava, A. Bansil, H. Lin, and M. Z. Hasan, Nat. Phys. 7, 32 (2011).
[21] R. Yu, W. Zhang, H.-J. Zhang, S.-C. Zhang, X. Dai, and Z. Fang, Science 329, 61 (2010).