Supplemental Material to the article

"Features of Electronic Structure of Topological Insulator Bi_2Se_3 Digitally Doped by the Atoms of $3d$ Transition Metals"

Calculational details. Our calculations of electronic properties of $(Bi_{2(1-x)}Me_{2x}Se_3)/(Bi_2Se_3)_n$ with $x = 0.5\ \ 1.0$, $n = 1{-}5$, 8 and Me = V, Cr, Mn, Fe, Co were performed by using the fully relativistic APW + lo method as implemented in WIEN2k code [1]. The exchange-correlation effects were described within the generalized gradient approximations (GGA). The $5d$ states of Bi are included in the APW basis set and treated as the valence orbitals. Density-functional calculations presented here were performed within the supercells. Converged results are obtained at the cut-off energy for the interstitial plane-wave expansion of 500 eV. Relaxations of all atomic positions were included in our calculations by using different computational scheme which employs the plane wave pseudopotential method VASP [2] and is significantly faster than that of WIEN2k. We used the local density approximation (LDA) for these relaxations, because it provides a convenient way for obtaining a realistic structure, while GGA often does not give realistic structures for the van der Waals bonded materials (see [3], and references therein). Relaxed atomic positions at the experimental lattice constants of bulk Bi_2Se_3 [4] first were found by the VASP, then were used as input in WIEN2k computation for the final atomic relaxations and the following calculation of spectral and magnetic properties. To verify relaxed geometries, the DOS and the local spin moments of $3d$ transition metals, a series of complete WIEN2k calculations were made. The results of the two types of computations (the combined VASP + WIEN2k approach and the WIEN2k method alone) were nearly identical. This agreement indicates that the computational parameters of both methods were properly fitted. Once structures were determined, we used the GGA for the electronic structure and optical calculations. Spin-orbit coupling was included in all the calculations except structure relaxations. We used a k-point sampling of $10 \times 10 \times 1$ for the total energy calculations and a **k**-mesh of $32 \times 32 \times 3$ for calculations of spectral properties.

Graphical illustration of Table 1 in the main text.

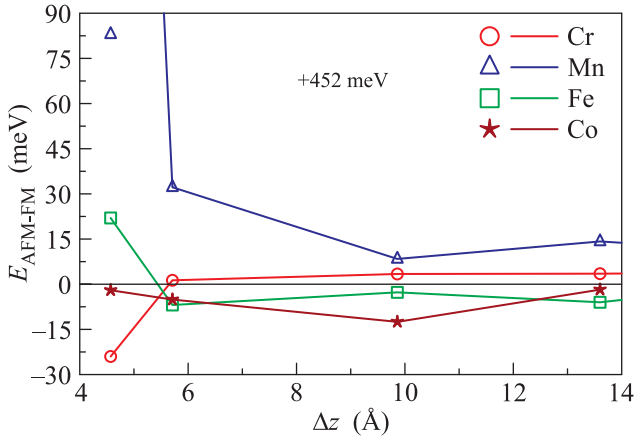

Figure 1: Figure S1. Magnetic energy ($E_{\text{AFM}} - E_{\text{FM}}$) as a function of distance between pair of doped transition atoms (Δz)

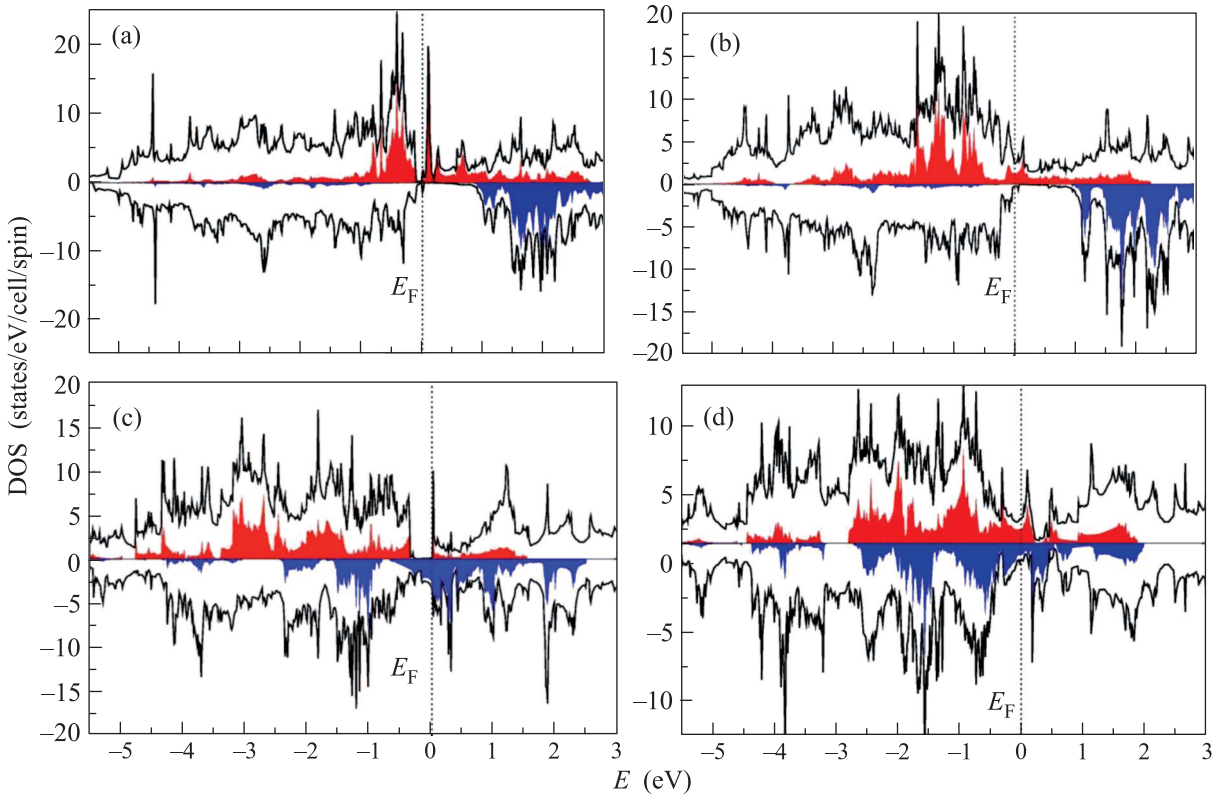

Figure 2: Figure S2. Density of states in $Me_2Se_3/(Bi_2Se_3)_2$: (a) – Me = V; (b) – Me = Cr; (c) – Me = Fe; (d) – Me = Co. Black lines are total DOS's, red and blue fillings are contributions to DOS of the Me $3d$-states with spin up and spin down, respectively

Analytical model of magnetic delta-insertion in three-dimensional topological insulator. In order to gain a deeper understanding of the DFT study results of the magnetic modulation doped topological insulators (TIs), we explore electron characteristics of a digital alloy within the framework of an analytical scheme of an isolated delta-insertion. Herein we imply that one of the quintuple layers of the Bi_2Se_3-like material host is enriched in $3d$-transition metal (TM) atoms replacing Bi atoms. Such a delta-insertion is treated as an ideal two-dimensional plane of dopant atoms. It is described on basis of the Anderson layer model (a two-dimensional analogue of the the Anderson impurity model [5]), which supposes that quasiparticles of the TI host are subject to a resonant scattering at d-states of TM atoms. The corresponding Hamiltonian reads $H = \sum\limits_{\vec{\kappa}} \hat{H}(\vec{\kappa})$, where:

$$\hat{H}(\vec{\kappa}) = \sum_{k,\sigma\sigma',\tau\tau'} H^{(TI)}_{\sigma\sigma'\tau\tau'}(\mathbf{k}) p^{+}_{\sigma\tau\mathbf{k}} p_{\sigma'\tau'\mathbf{k}} + \sum_{\sigma} \varepsilon^{d} d^{+}_{\sigma\vec{\kappa}} d_{\sigma\vec{\kappa}} + \sum_{k_z,\sigma,\tau} (V_\tau d^{+}_{\sigma\vec{\kappa}} p_{\sigma\tau\mathbf{k}} + h.c.) + \sum_{k_z,k'_z,\sigma,\tau} W_\tau p^{+}_{\sigma\tau\mathbf{k}} p_{\sigma\tau\mathbf{k}'}. \quad \text{(S1)}$$

The 4×4 Hamiltonian of the three-dimensional TI bulk, $H^{(TI)}$, is represented in the minimal basis, $u_\Gamma = \{|+\uparrow\rangle, |-\uparrow\rangle, |+\downarrow\rangle, |-\downarrow\rangle\}$, formed by four low-energy states differing in parity (+ or −) and spin projection (↑ or ↓) onto the $\mathbf{z}$ quantization axis as it is inherent to the band model of the semiconductor materials of Bi_2Se_3-type near the Γ point [6]. Within the $\mathbf{k}\cdot\mathbf{p}$ method, it is given by the standard expression:

$$H^{(TI)}(\mathbf{k}) = (\Xi - Bk^2)\tau_z \otimes \sigma_0 + A\tau_x \otimes (\vec{\sigma}\cdot\mathbf{k}), \quad \text{(S2)}$$

where $\mathbf{k} = (k_x, k_y, k_z)$ is a momentum measured from the Γ point, σ_α and τ_β $(\alpha, \beta = 0, x, y, z)$ denote the Pauli matrices in the spin and orbital space, respectively. For the sake of simplicity, we assume that the system is

isotropic and the electron and hole branches are symmetric. The condition $\Xi\,\mathrm{B} > 0$ determines the inverted order in energy of the basis states around $\mathbf{k} = 0$ due to strong spin orbit coupling. The spin and orbital degrees of freedom are indexed as $\sigma, \sigma' = \uparrow, \downarrow$ and $\tau, \tau' = +, -$, respectively. In Equation (S1) the operator $p^{+}_{\sigma\tau\mathbf{k}}$ [$p_{\sigma\tau\mathbf{k}}$] creates [annihilates] particle in the band τ with momentum $\mathbf{k}$ and spin projection σ. The operator $d^{+}_{\sigma\vec{\kappa}}$ [$d_{\sigma\vec{\kappa}}$] creates [annihilates] particle with longitudinal momentum $\vec{\kappa} = (k_x, k_y)$ and spin projection σ inside the delta-insertion.

We study the case of a single d-orbital at TM atom. In other words, we exclude possibility for the higher value of the atom spin, resulting from Hund's rule within the d-orbital, which does not play an important role in our consideration. Moreover, we neglect a direct overlap between the d-orbitals belonged to different cites occupied by TM atoms as they are rather far apart. Therefore, the initial state of the insertion is dispersionless with an energy level ε^d. However, d-electrons become mobile along the insertion plane due to the hybridization V_τ with the orbitals of the TI host. The last term in Eq. (S1), proportional to W_τ, determines the electrostatic potential modulation caused by a charge density redistribution in the TI host around the delta-insertion. The aforesaid effect do not break the translation invariance along the insertion.

The Coulomb repulsion at the same d-orbital is usually the dominant energy scale and, hence, can be the driving force of magnetism. The introduction of the Hubbard-type electron correlations at the TM cite leads to a spin splitting of the initial state, $\varepsilon^d_\sigma = \varepsilon^d + U\langle n^d_{-\sigma}\rangle$, where $\langle n^d_\sigma\rangle$ is the average number of electrons with spin σ at the d-orbital, U is the Coulomb repulsion energy. We assume that the magnetic moments in the spin-polarized state are perpendicular to the insertion plane. By using the Green functions technique, one obtains the full t-matrix of multiple scattering of electrons by the delta-insertion. The t-matrix poles determine the two-dimensional bound states induced by the insertion. We focus on the situation $\varepsilon^d < \mu < \varepsilon^d + U\langle n^d_\downarrow\rangle$ (where μ is the chemical potential level), which corresponds to our DFT investigation of TI Bi2Se3 discretely doped with such TMs as Mn, Cr and V. One supposes that the level ε^d lies well below the valence band edge of the TI host as compared with the hybridization smearing of the level, i.e., $\Xi - \varepsilon^d \gg \gamma \sim |V_\tau|^2$, and the interaction U is strong enough, $\varepsilon^d + U\langle n^d_\downarrow\rangle - \Xi \gg \gamma$. Then just one electron occupies the d-state at TM atom: $\langle n^d_\uparrow\rangle = 1$ and $\langle n^d_\downarrow\rangle = 0$. Under these stipulations, one can construct two pairs of the effective dimensionless potentials, $u_{\uparrow\tau} = \frac{ak_0|V_\tau|^2}{2\Xi|\varepsilon^d|}$, $u_{\downarrow\tau} = \frac{ak_0|V_\tau|^2}{2\Xi\varepsilon^d + U}$, where a is a lattice constant, $k_0 = \sqrt{\Xi/2B}$. Correspondingly, there are two pairs of the low-energy spin-polarized states that are induced by the delta-insertion. When $W_\tau = 0$, we can explicitly describe the spectra of these states, $\omega_{\sigma\tau}(\kappa)$. The relatively weak potential, $u_{\uparrow-} \ll 1$ ($u_{\downarrow+} \ll 1$), splits off the spin-up (-down) state with $\Xi + \omega_{\uparrow-} \sim u^2_{\downarrow-}$ ($\Xi - \omega_{\downarrow+} \sim u^2 +_{\downarrow+}$) from the valence (conduction) band. To split off another state with the same spin from the band continuum, the finite strength potential is required, $u^2_{\uparrow+}$, $u^2_{\downarrow-} \geq \chi - 1$, where $\chi \equiv \mathrm{A}^2/2\mathrm{B}\Xi > 1$. In the case of the strong potential, $u_{\sigma\tau} \gg 1$, the four spectral branches with parabolic dispersion appear inside the TI gap near $\kappa = 0$:

$$\omega_{\uparrow\tau}(\kappa) = -|\mathrm{A}|k_0\left[u^{-1}_{\uparrow\tau} + \frac{(\kappa/k_0)^2}{u^{-1}_{\uparrow\tau} + u^{-1}_{\downarrow-\tau}}\right], \quad \omega_{\downarrow\tau}(\kappa) = -|\mathrm{A}|k_0\left[u^{-1}_{\downarrow\tau} + \frac{(\kappa/k_0)^2}{u^{-1}_{\uparrow-\tau} + u^{-1}_{\downarrow\tau}}\right], \tag{S3}$$

If the momentum is large, $\kappa > k_0 u^{-1}_{\sigma\tau}$, these branches are described by the Dirac spectrum: $\omega_{\uparrow\tau}(\kappa) = -|\mathrm{A}|\kappa$ and $\omega_{\downarrow\tau}(\kappa) = |\mathrm{A}|\kappa$.

In this simple model, choosing the typical values for the material parameters of the TI host and the delta-insertion, $|\mathrm{A}| = 0.2\,\mathrm{eV{\cdot}nm}$, $\mathrm{B} = 0.5\,\mathrm{eV{\cdot}nm^2}$, $\Xi = 0.2\,\mathrm{eV}$, $a = 1\,\mathrm{nm}$, $\varepsilon^d \approx -3\,\mathrm{eV}$, $\varepsilon^d + U \approx 1\,\mathrm{eV}$, $|V_\tau| = 2\,\mathrm{eV}$, we arrive at the following estimations: $u_{\uparrow\tau} = 1.2$, $u_{\downarrow\tau} \approx 4$, $\omega_{\uparrow\tau}(0) = -0.06\,\mathrm{eV}$, $\omega_{\downarrow\tau}(0) = -0.02\,\mathrm{eV}$. Thus, the induced states with small κ reside deep inside the gap, $|\omega_{\sigma\tau}(\kappa)| \ll \Xi$, and are strongly localized near the insertion to a thin region $\sim k_0^{-1} \approx 2\,\mathrm{nm}$. However, the switching on of the electrostatic potential, $W_\tau \neq 0$, produces an energy shift of the induced states in relation to $\omega_{\sigma\tau}(\kappa)$ (S3) so that they can leave the gap merging into the bulk band continuum. The similar effect appears at the boundary between TI and trivial insulator, where the interface potential modifies the bound states [7].

References

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