Photoemission Spectroscopy of Magnetic and Non-magnetic Impurities on the Surface of the Bi$_2$Se$_3$ Topological Insulator

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The single crystal samples were synthesized by mixing stoichiometric amounts of bismuth and selenium with...
trace amounts of arsenic in evacuated quartz tubes [24]. The ARPES experiments were carried out at the U13UB beamline of the National Synchrotron Light Source with the photons in the range between 15.5 and 22 eV. The electron analyzer was a Scienta SES-2002 with the combined energy resolution around 8 meV and the angular resolution of \( \sim 0.15^\circ \). Samples were cleaved in-situ in the UHV chamber with the base pressure of \( 3 \times 10^{-9} \) Pa. Ni was deposited using an e-beam evaporator, Cu and Gd were evaporated from a resistively heated tungsten basket, while alkalies were deposited from commercial (SAES) getter sources with the samples kept at \( \sim 15 \) K during the deposition and ARPES measurements.

Figure 1 shows the development of surface electronic structure upon deposition of rubidium on the \( \text{Bi}_2\text{Se}_3 \) surface. The rapidly dispersing conical band in the pristine sample represents the TSS with the Dirac point around 0.32 eV below the Fermi level. At binding energy higher than 0.4 eV the TSS overlaps with the bulk valence band (BVB) and near the Fermi level, the bulk conducting band (BCB) is visible inside the surface state cone, indicating the electron doping of \( \text{Bi}_2\text{Se}_3 \) by Se vacancies. The TSS has an almost perfectly circular Fermi surface. Upon Rb deposition, TSS is further doped with electrons, evident from the down-shift of the Dirac point and the growing Fermi surface that acquires a pronounced hexagonal warping. However, this is not the only effect of doping: new states are also being formed and progressively filled with electrons donated by adsorbed Rb. In panels c) and d) we show the stage of Rb deposition at which the maximal charge transfer into the surface electronic structure of \( \text{Bi}_2\text{Se}_3 \) is reached. At this stage, in addition to the original TSS, two pairs of new states are visible at lower binding energies. Each pair consists of two spin-orbit split states, displaced in momentum in a Rashba-type manner, intersecting at new Dirac points at the zone center. These states also have surface character as they do not disperse with \( k_z \). At the highest doping levels, the outermost state becomes almost degenerate with the TSS, forming the Fermi surface nearly equal in shape and size. Its inner counterpart is significantly smaller, retaining the perfectly circular Fermi surface, even at the highest doping. We also observe new valence states below the Dirac point of the TSS. Although their dispersion near the zone center resembles the dispersion of the BVB, the lack of \( k_z \) dispersion indicates their surface character.

Fig. 1e) summarizes the changes in some of the measured quantities with Rb doping. The surface doping level was determined by measuring the Fermi surface area of the TSS and of the lower Rashba-split doublet: \( A_T \) (TSS), \( A_O \) (outer Rashba state) and \( A_I \) (inner Rashba state). The upper Rashba doublet was not taken into account. The total charge (per surface unit cell) is then \( q = (A_T + A_O + A_I)/A_{BZ} \), where \( A_{BZ} = 2.602 \) \( \text{Å}^{-2} \) represents the Brillouin zone area. At maximal doping, nearly 0.105 \( e^- \) per surface unit cell is transferred from Rb into the three states shown here. If the second pair of states (better resolved in Fig. 2c) is counted, then the total charge transfer is \( \sim 0.14 \) \( e^- \). The surface charge density \( n = q/A_{UC} \), where \( A_{UC} = 44.487 \) \( \text{Å}^2 \) is the area of the unit cell in real space, could be tuned from \( \sim 1 \times 10^{12} \) \( \text{cm}^{-2} \) (clean sample) to \( \sim 5 \times 10^{13} \) \( \text{cm}^{-2} \) (maximal doping). As a Rb atom can donate at most one electron, the measured charge transfer implies that the average Rb-Rb distance could be shorter than 3 unit cells. Scattering on Rb would then lead to the very short mean free path for surface electrons (\( \sim 3 \) surface unit cells). However, Fig. 1 suggests that all the states are still very coherent, with the mean free paths \( \ell = 1/\Delta k \) in the range of 100 \( \text{Å} \), where \( \Delta k \) is the momentum spread of the Fermi sur-

FIG. 1: Surface doping of \( \text{Bi}_2\text{Se}_3 \). a) to d) ARPES spectra from \( \text{Bi}_2\text{Se}_3 \) at various stages of Rb deposition, showing the Fermi surface (upper panels) and the \((E,k)\) dispersion of photoemission intensity along the momentum line slightly off the \( \Gamma M \) line in the surface Brillouin zone (lower panels). a) pristine surface, b) intermediate doping and c) maximal doping, taken at \( h\nu = 21.3 \) eV and at \( h\nu = 18.7 \) eV (d). e) Fermi surface area of the TSS and of the lower Rashba doublet (bottom), charge doped into these states (middle) and work function (top) as functions of Rb deposition time.
FIG. 2: Development of the surface electronic structure with Cesium (a), Gadolinium (b) and Rubidium (c) adsorption at the surface of $\text{Bi}_2\text{Se}_3$. The spectra were recorded along the $\Gamma M$ line in the surface Brillouin zone and at $h\nu = 18.7 \text{ eV}$ for Cs and Gd and along $\Gamma K$ line and at $h\nu = 21.3 \text{ eV}$ for Rb. The leftmost panels correspond to the pristine surface, while the rightmost panels show the electronic structure near the maximal doping achieved with each dopant.

The most important observation from the spectra in Fig. 2 is that, contrary to the expectations, the magnetic state of the adsorbate does not seem to play a significant role in the scattering. At similar stages of doping with different adsorbates, the TSS seems similarly coherent. The same is true for the Rashba-split states. Further, it appears that all the adsorbates have a similar effect on the spectral region around the Dirac point of TSS, with no clear gap formation.

In Fig. 3 we show the imaginary part of the quasiparticle self-energy, $\text{Im}\Sigma(\omega) = \Gamma(\omega)/2$, where $\Gamma(\omega)$ represents the scattering rate, as a function of binding energy for TSS for several different concentrations of Rb and Gd atoms on the surface of $\text{Bi}_2\text{Se}_3$. Scattering rates are determined from $\Gamma(\omega) = 2|\text{Im}\Sigma(\omega)| = \Delta k(\omega)v_0(\omega)$, where $\Delta k(\omega)$ is the measured full width at half maximum of the Lorentzian-fitted peak in MDC, and $v_0(\omega)$ is the group velocity of the state at energy $\omega$. The TSS remains very coherent until the concentration of adsorbed atoms reaches the level at which the Fermi surface becomes heavily hexagonally warped, regardless of whether the adsorbates are magnetic or non-magnetic. For similar doping levels, the scattering rates are essentially the same for Rb and Gd covered surfaces. Pristine surfaces and surfaces with relatively low concentration of impurities, show very low $\text{Im}\Sigma$ at the Fermi level, indicating long coherence lengths of TSS, $\ell > 150 \text{ Å}$. Even at the doping levels $\sim 0.05 \text{ e}^-/\text{surface unit cell}$, where the average distance between the impurities is shorter than $\sim 5 \text{ unit cells}$, the TSS remains unaffected. $\text{Im}\Sigma$ slowly increases with energy as $\propto \omega^2$, indicating that the inelastic electron-electron scattering has a Fermi-liquid-like form. For high impurity concentrations, $\sim 0.1 \text{ e}^-/\text{surface unit cell}$, $\text{Im}\Sigma$ reaches the value of $\sim 40 \text{ meV}$ at
The Fermi level, corresponding to the mean free path of \( \sim 70 \text{ Å} \), and is nearly energy independent. Due to the partial overlap with the significantly more intense outer Rashba state, we could not reliably determine the width of the TSS at low energies. We also show the \( \Im \Sigma \) for the two states that form the lower Rashba-split doublet. There is a significant difference between the states forming the doublet: the outer state is significantly broader than the inner one and is similar in width to the TSS at this concentration level. This is again true for both magnetic and non-magnetic impurities.

In Fig. 4 we illustrate the effects of Cs and Gd deposition on the spectral region near the Dirac point of TSS. We show the spectral intensity at the point slightly displaced from the \( k_z = 0 \) (middle panels) and exactly at the \( k_z = 0 \) point (right panels), as a function of Cs and Gd deposition time. Contrary to the expectations, both metals have similar effects: with the deposition of these metals, it seems as if the lower and the upper parts of the Dirac cone penetrate each other. Thus, at small but finite \( k_z \), the two branches merge and possibly intersect after \( \sim 6 \text{ min} \) of evaporation. If the gap opens at the Dirac point, as might be expected for magnetic impurities, the upper and the lower branch of the TSS cone should remain separated. The separation should also occur at \( k_z = 0 \), once the gap opens. Our results suggest that neither of the adsorbates opens a clear gap at the Dirac point of the TSS. We also see no evidence of a gap at the second Dirac point, where the states forming the lower Rashba-split doublet intersect (Fig. 2). This suggests that the Kramer’s points, i.e. the points where the spins are degenerated in the unperturbed system, are more robust to magnetic perturbations than expected. One possible reason for this insensitivity could be a strongly localized magnetic moment (\( f \) orbitals) in adsorbed Gd, resulting in a very small scattering cross-section. However, similar results for adsorbed nickel and iron \[17\] with the more delocalized moments, would argue against this explanation.

Our experiments show that the quasi-particle scattering on the surface of a TI is not affected by magnetic moments of impurity atoms. This might imply that the scattering rates are dominated by the small momentum transfer events and not by back-scattering. Then, the existence of multiple Fermi surfaces, allowing both the intra-band and inter-band scattering, and the observation that the inner Rashba-split Fermi surface is always sharper than its outer counterpart and the TSS might suggest that the former one has the opposite spin helicity than the latter two. However, recent calculations \[17\] suggest that the spin helicities of these three states alternate (L-R-L). If this is the case, our results would imply that the inter-band scattering is strongly suppressed. Indeed, we do not see any anomalies in the scattering rates at the thresholds for the inter-band channels. Therefore, we could conclude that the observed broadening with adsorption of impurities reflects the increase in intra-band scattering as the size and the warping of the Fermi surface grows with doping \[9, 11, 13, 26, 27\]. We note that these effects will likely play determining role in a performance of any electronic device based on a topological insulator, because any environmental doping will inevitably affect the surface state mobility, \( \mu_S = e\ell_{tr}/(\hbar v_F) \), in transport experiments. Even though the transport mean free path, \( \ell_{tr} \), might be significantly longer than \( \ell \), especially when back-scattering is suppressed, our results indicate that mobilities will be reduced by the doping, implying that the full potential of TIs could only be realized in a controlled, preferably ultra-high vacuum environment, or by an inert capping of the surface.

In conclusion, we have observed that magnetic moment of an impurity does not play a dominant role in the scattering of the TSS. However, with the increasing doping, the state becomes warped, and the scattering eventually increases - irrespective of impurity’s magnetic moment. Therefore, the TSS does not remain protected.
indefinitely, even when doped with non-magnetic impurities. Further, we have not seen any difference in the spectral region around the Dirac point between magnetic and non-magnetic adsorbates, questioning previous claims that the observed spectral features indicate a magnetism-induced gap [17].

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