Article Subject (see Index Terms below and write one here)

Femtosecond dynamics of spin-polarized electrons in topological insulators

H. Hedayat[1], D. Bugini[1], H. Yi[2], C. Chen[2], X. Zhou[2], G. Cerullo[1], C. Dallera[1], E. Carpene[3*]

[1]*Dipartimento di Fisica, Politecnico di Milano, 20133 Milan, Italy*

[2]*National Lab for Superconductivity, Institute of Physics, Chinese Academy of Science, Beijing 100190, China*

[3]*CNR-IFN, Dipartimento di Fisica, Politecnico di Milano, 20133 Milan, Italy*

Received 2017, accepted , published, current version 2017. (Dates will be inserted by IEEE; "published" is the date the accepted preprint is posted on IEEE Xplore®; "current version" is the date the typeset version is posted on Xplore®).

Abstract— A faster control of spins is a major request for the new generation of computing and spintronic systems. In this framework, since many years, ultrashort light pulses have been utilized to trigger and detect the spin dynamics of electrons in magnetic materials and multilayers. Recently, three-dimensional topological insulators (TIs) have received attention in the field of spintronics due to their spectacular features, in particular, the existence, within the insulating gap of bulk states, of spin-polarized surface states (Dirac-cone) that are protected from backscattering by time-reversal symmetry. We have studied the sub-picosecond dynamics in the spin-polarized unoccupied electronic structure of Bi_2Te_3, employing circular-polarized light in time and angle resolved photoemission spectroscopy (trARPES). Exploiting the noncollinear optical parametric amplification (NOPA) besides several nonlinear optical processes resulted in tunable ultrashort visible pump pulses with 30 fs length and 1.8 eV energy and ultraviolet probe pulses with about 6 eV and 60 fs. The stable optical setup and the high repetition rate of an Yb-laser source grants a high signal-to-noise ratio in our photoemission process. The obtained 65 fs time resolution, along with 30 meV energy resolution of the time-of-flight (TOF) energy analyzer, provides us with an exciting possibility to explore the ultrafast electronic dynamics in the unoccupied band structures. Furthermore, circular dichroism (CD) allows access to the spin state of the photoemitted electrons. We found a signature of femtosecond unpolarized bulk bands dynamics in the presence of spin-polarized electrons of the surface states. This observation aided to distinguish the bulk and surface contributions in the spin-electronic current.

Index Terms— Topological insulators, Spin dynamics, Photoemission spectroscopy, Circular dichroism, trARPES, Bi_2Te_3

I. INTRODUCTION

Review Using the spin of electrons, in addition to their charge, can revolutionize electronic and computing systems to deliver expanded performances [Wolf 2001, Awschalom 2013]. Over the last decades, many theoretical and experimental investigations on electronic structures and dynamics have focused on this technological mission [Ostler 2012, Beaurepaire 1996, Kirilyuk 2010, Carpene 2008, Fan 2014]. In this framework, the exotic properties of three dimensional topological insulators (3D TIs) have attracted tremendous attention. TIs are promising materials for the emerging field of ultrafast spintronics owing to their helical spin-polarized topological surface states (TSSs) located within the insulating unpolarized bulk band (BB) gap [Hsieh2008, Hsieh 2009, Moore 2010] and characterized by an extraordinary backscattering resistance [Zhang 2009, Roushan 2009]. In the preliminary studies, the spin generation, manipulation and control was attributed to surface-related phenomena, and the contribution from bulk states was largely obscure. More recently, detailed investigations on unpolarized BBs have led to a more profound understanding of the spin configuration in TIs. For example, the induced Rashba splitting effect and the generation of spin current in BBs are well-established phenomena [Zhu 2011, Wray 2011, Hsieh 2011]. It has recently been discovered that the spectral weight of BBs is reduced in the surface vicinity in favor of the surface resonance (SR) states. SRs are spin polarized states with opposite spin direction with respect to TSSs [Cacho 2015, Jozwiak 2016]. Nonetheless, a careful distinction between the spin structure and ultrafast dynamics of bulk and surface states remains a crucial experimental challenge.

Angle resolved photoemission spectroscopy (ARPES) has been the key technique to disclose the electronic structure of TIs [Chen 2010]. Combining ARPES with other experimental methods can provide additional information on electronic dynamics and spin states. In time-resolved ARPES (trARPES), an ultrafast intense laser pulse, the pump, brings the electronic system out-of-equilibrium [Sobota 2012, Wang 2012, Bugini 2017]. Thus, one can access unoccupied bands which after pump excitation are filled with hot electrons. The time evolution of their excitation and relaxation can provide valuable information on the possible particle and quasi-particle interactions in TIs band structure. In circular dichroism ARPES (CD-ARPES), the momentum of circularly polarized probe photons couples with the angular momentum of electrons [Wang 2011, Park 2012, Jung 2011]. The difference in the photoemission intensity of each circular probe

* Corresponding author: E. Carpene (ettore.carpene@polimi.it)

Digital Object Identifier: 10.1109/LMAG.XXXX.XXXXXXX (inserted by IEEE).

helicity (Right Circular Light, RCL or Left Circular Light, LCL) contains the relevant spin information. The combination of all described techniques, i.e. trCD-ARPES, can be employed to elucidate the spin-electron dynamics in the unoccupied electronic structure.

In this letter, we present trCD-ARPES results revealing the unoccupied spin-electronic structure of Bi_2Te_3. Our results show that the CD contrast of the surface resonance (SR) state in the empty BBs displays opposite spin direction with respect to TSS. Moreover, the dynamical CD analysis shows the different behavior of spin polarized and unpolarized electrons after photoexcitation. The effect is attributed to a spin current or spin accumulation in the BBs and SR states, accompanied by different dynamics of the unpolarized electrons.

II. MATERIALS AND EXPERIMENTAL METHODS

A. Synthesis of Bi_2Te_3

Bi_2Te_3 single crystals were grown by the self-flux method. The high-purity raw materials were mixed according to the compound stoichiometry. The specimens were heated to 1000 °C for 12 hours then, gradually cooled down to 500 °C over 100 hours. The samples were cleaved and measured at room temperature in ultrahigh vacuum with pressure better than 5×10^{-10} mbar.

B. TrCD-ARPES system

Fig. 1 shows a schematic view of the experimental trCD-ARPES apparatus. The laser source is a commercial regeneratively amplified mode-locked Yb:KGW system delivering pulses at 100 kHz repetition rate with 1030 nm central wavelength and 300 fs duration. The fundamental beam (FB) is split into two main parts. A fraction of the pulses is used to generate ultrashort visible tunable pulses, the pump, spanning the 620–720 nm wavelength range, through a compressed noncollinear optical parametric amplification (NOPA). The other fraction of FB is directed to the sum-frequency generation (SFG) part, where the deep ultraviolet probe with about 200 nm wavelength and 65 fs duration is generated. Using a quarter waveplate, the circular helicity of the probe is carefully adjusted. The time evolution is attained by changing the delay between pump and probe pulses on the sample surface (delay stage in Fig. 1). The time of flight (ToF) spectrometer, is used to extract the energy of the photoemitted electrons on a micro channel plate (MCP). More details about the ToF system and the optical layout can be found in [Carpene 2009, Boschini 2015]. Our trARPES system provides a high signal-to-noise ratio with about 70 fs time and 40 meV energy resolutions.

III. RESULTS AND DISCUSSION

To study the pump-induced dynamics of the unoccupied electronic and spin structures, we performed CD-ARPES measurements vs pump and probe delay. Fig. 2 (a)-(c) show the data along the $\overline{\Gamma K}$ direction, in equilibrium (a, un-pumped) and at delays of 250 (b) and 1000 (c) fs after optical excitation with 1.8 eV linear-polarized photons.

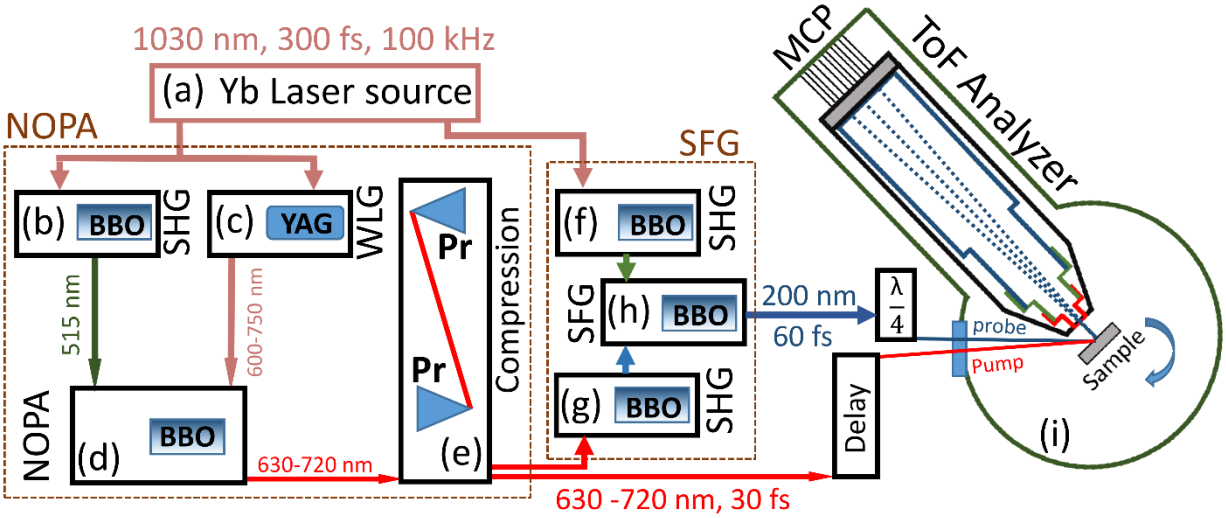

Fig. 1. Schematic drawing of the in house - developed system to measure trCD-ARPES. (a) a Yb:KGW laser source (b) second harmonic generation (SHG) doubling the laser fundamental frequency, (c) white light supercontinuum (WLC) generated inside a YAG crystal. (d) WLC seed pumped 515 nm beam focused inside a 2 mm BBO crystal generating the ultrabroadband NOPA signal. (d) NOPA dispersed by a pair prism (Pr) compressor. The output compressed NOPA is then split. One portion goes to a motorized delay stage and is directly used as ultrashort tunable pump. The other fraction is frequency doubled in (f) to generate the ultraviolet probe. In (g), the 515 nm beam (e) and the SHG 335 nm beam(f) generate the 203 nm probe beam in a sum frequency generation (SFG) process. The probe goes through quarter-wave plate and is focused on the sample (h) shows the ultrahigh vacuum photoemission chamber, equipped with a time of flight (ToF) analyzer. The ToF records the flight-time of the photoelectrons collected by micro channel plate (MCP) detector.

The left panels show the band structure at different delays, the right panels are the corresponding CD measurements. The dichroic contrast is calculated as the normalized difference of the ARPES maps measured with probe of opposite helicities, i.e. CD = (RCL-LCL)/(RCL+LCL). We start from the description of the left panels. In Fig. 2(a) we see the band structure in equilibrium condition, with the occupied bulk valence band and the partially occupied Dirac-cone. Fig. 2(b) shows the bands 250 fs after photoexcitation. The empty part of TSS is populated and two bulk bands (BB1 and BB2) are filled at higher energies. The lower-lying bulk band (BB2) has a parabolic dispersion and is observed in proximity of the linearly dispersing TSS (see the dashed line as a guide). BB1 empties within the first picosecond, while BB2 and TSS are further filled by electrons decaying from higher energy Fig. 1(c)-left. The observed electronic dynamics is consistent with previous investigations [Hajlaoui 2011].

The CD associated with the observed states is shown in the right panels of Fig. 2. Fig. 1(b) shows that both bulk and surface states display a CD signal. Moreover, the CD of all bands changes sign when crossing the center of the first Brillouin zone, $\bar{\Gamma}$. The CD from the BBs has opposite sign with respect to the neighboring branch of TSS. The BBs are generally considered unpolarized, but our observation of a sizable CD reveals the presence of spin polarized electrons. As anticipated in the introduction, recent theoretical and experimental observations demonstrated the existence of the surface resonance (SR) in the nearby BBs with antiparallel spin direction with respect to TSSs [Cacho 2015, Jozwiak 2016]. Our CD measurements agree with the spin structure of Bi_2Te_3 recently reported in [Sánchez-Barriga 2017]. Therefore, the origin of the CD in BB1 and BB2 can be explained by the SR spin texture. Another possible explanation for the presence of spin polarized electrons in the BBs is the existence of a spin-polarized electronic dynamics in unpolarized states. It is well known that the excitation of TIs with a linear pulse results in a constant spin configuration of the TSS dynamics due to the momentum symmetric population of TSS, its robust spin structure and to the lack of backscattering events. Instead, in BBs the optical excitation cannot generate a constant spin polarization dynamics, because of spin-unpolarized states and the unpolarized charge dynamics. The presence of an invariable spin dynamics in BBs would demonstrate that the BBs are spin polarized like TSS. But finding a spin dynamics distinguishable from the unpolarized electronic dynamics demonstrates diverse scattering channels of BBs, whose origin may require further investigation.

We explored the sub-picosecond time and spin evolution of two energy-momentum regions shown in Fig. 2(c) (small boxes in the left panel) corresponding to the TSS and BB2 regions, respectively. We compared the electronic dynamics of each band by looking at the time-dependent CD and at the difference (DIFF) in intensity for opposite circular-probe lights. DIFF is defined as the non-normalized CD (DIFF = RCL-LCL). Thus, similar to CD, a non-zero DIFF indicates the spin orientation of electrons, but, unlike CD, DIFF is not proportional to the spin polarization. If the dynamics of electrons and DIFF are analogous, then CD would be time independent. A time invariant CD signal is expected in a spin polarized band since the spin polarization is constant regardless of the band population. Fig. 3(a)

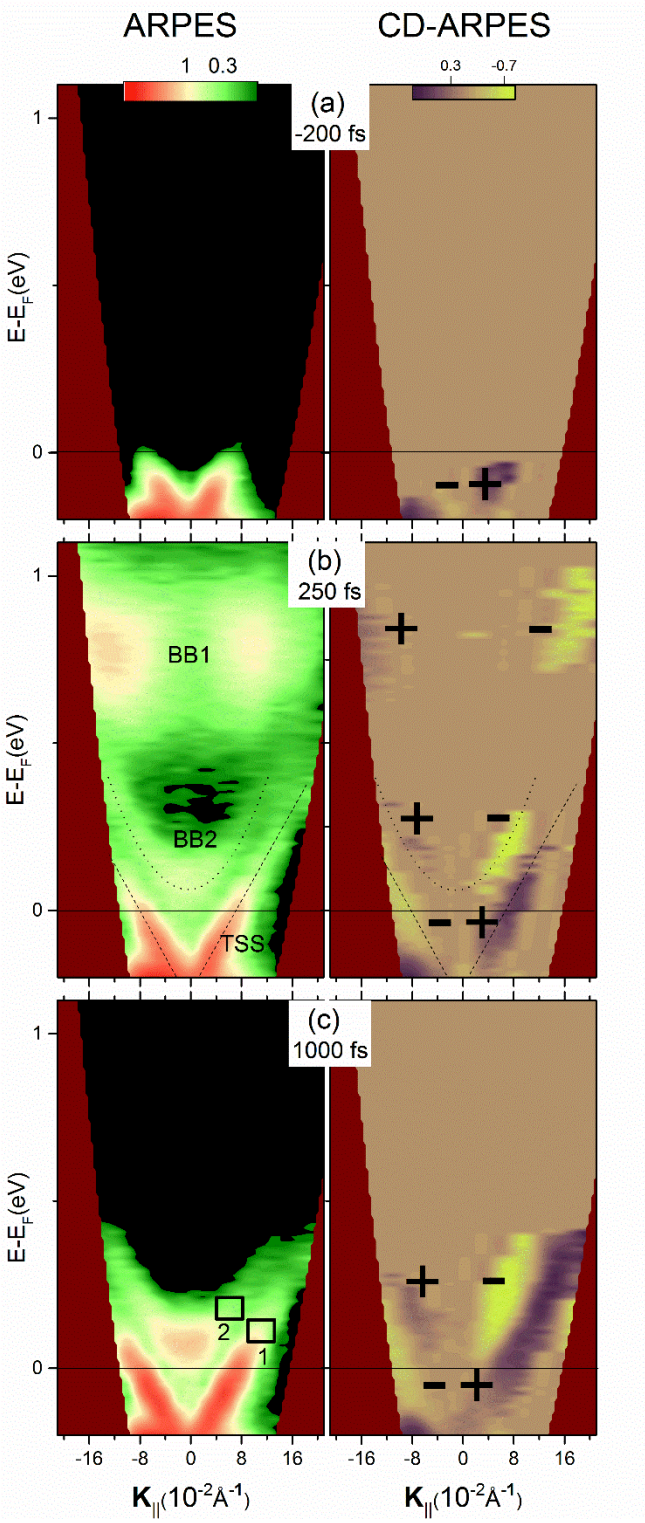

Fig. 2. Left panels present the ARPES data on Bi_2Te_3 along the $\bar{\Gamma}\bar{K}$ direction, in equilibrium (a) and at a delay of 250 fs (b) and 1000 fs (c) after the optical excitation. In (b)-left, the dashed lines guide the eyes to follow the BB2 and TSS bands. Right panels show the corresponding extracted CD maps. Dark-blue and yellow colors represent the positive and negative CD signs for each band. The horizontal black line is the Fermi level. Two small boxes in (c)-left are the integration regions to extract the detailed dynamics of Fig. 3.

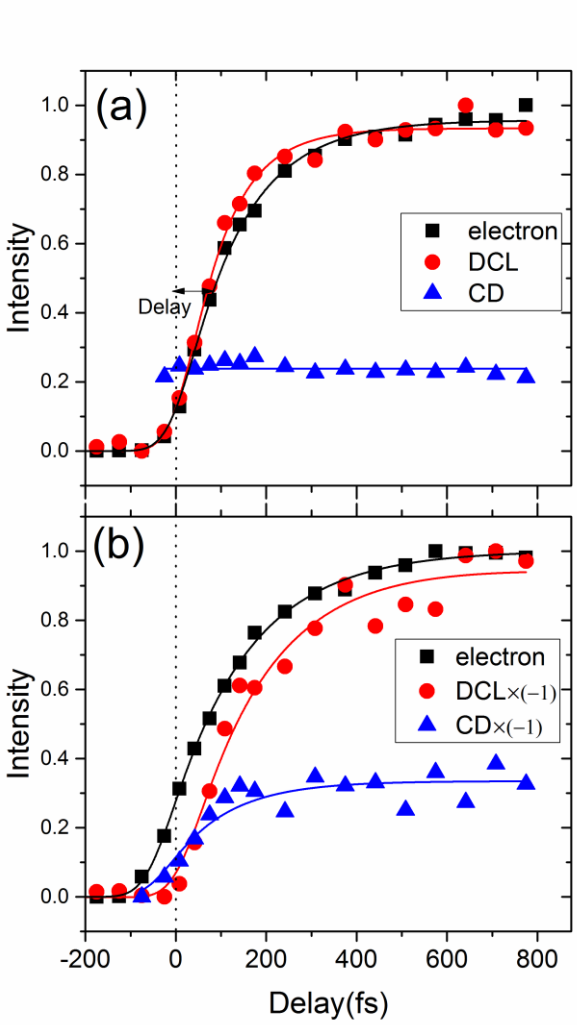

Fig. 3. (a) Sub-picosecond electronic (squares), DIFF (circles) and CD (triangles) dynamics of TSS, extracted from box 1 in Fig. 2(c)-left. DIFF and CD are defined as DIFF=(RCL-LCL) and CD=(RCL-LCL)/(RCL+ LCL). (b) Same dynamics as in (a) for BB2, box 2 in Fig. 2(c)-left. The CD of BB2 is negative and was multiplied by (-1) to ease comparison. The dashed lines show the pump and probe zero time. CD is not calculated for negative delays to avoid division by zero. The solid lines in (a) and (b) are exponential fits convoluted with the experimental time response, the CD of TSS was fitted with a constant function.

shows the time dependence of the electronic intensity (black square), DIFF (red circles) and CD (blue triangles) for TSS (box 1 in Fig. 2(c)-left). The electronic and DIFF dynamics are normalized to their respective maxima and fitted by exponential functions convoluted with the experimental response. Notice that CD data cannot be computed in the time region prior or close to pump excitation since the electronic population is negligible, resulting in a division by zero. The electronic dynamics (black squares) reveals that the TSS is populated after a noticeable delay (about 60 fs). This delay indicates that the TSS is not directly photoexcited by the pump photons, but filled by electronic relaxation from higher BBs. The corresponding DIFF dynamics closely follows the electronic variations, while the CD signal is almost constant, with a value of 0.237. Fig. 3 (b) shows the data obtained from the second energy-momentum region of Fig. 2 (c), i.e. the BB2. The electronic dynamics starts without appreciable delay and displays a gradual filling. The DIFF signal of BB2, in contrast with the case of TSS, does not follow the electronic dynamics (compare the squares and circles in Fig. 3(b)). The DIFF dynamics exhibit a significant delay (about 60 fs) and a rise-time (215 ± 41 fs) different with respect to electronic dynamics in BB2 (178 ± 7 fs, extracted from fitting). Likewise, the CD of BB2 varies in time (triangles in Fig. 3(b)). The different evolutions of the CD in TSS and BB2 reveals the different spin structure and dynamics of the bulk and surface states of TIs.

The TSS has spin-polarized electron states which are robustly locked to their momentum and constrain the filling electrons to a well-defined spin texture. Consequently, the spin polarization is preserved also when changing the pump-probe delay. The bulk states show a more complex spin dynamics: hot electrons in BBs have more scattering channels to lose their energy and spin information. But BBs at the surface show a preferred spin polarization opposite the TSS one. Thus, electrons cannot decay from BBs to TSSs due to the unavailability of spin states. These electrons with opposite spin can accumulate in BB2 and scatter away at larger time delays.

IV. CONCLUSIONS

In conclusion, we studied the spin structure of single crystalline Bi_2Te_3 by the trCD-ARPES technique. TrCD-ARPES provides direct access to time evolution, spin direction, energy and momentum of photoexcited electrons. For the first time, we reported the circular dichroism signal of the unoccupied electronic structure of Bi_2Te_3. Our results demonstrate the complex spin texture of TSS and BBs. The spin preference of BBs is attributed to the surface resonance states. Moreover, we investigated the femtosecond evolution of spins and electrons in TSS and BBs after excitation with a linearly polarized pump beam. As expected, a constant spin polarization was observed in TSS dynamics. The spin dynamics of BBs showed a qualitatively different behavior with respect to TSS. We assign this difference to the complex interplay of BBs with the surface, where the development of resonant states seems to be a fundamental ingredient.

ACKNOWLEDGMENT

This research is supported by Fondazione Cariplo (grant 2011-0389) and by Politecnico di Milano via the Interdepartmental Laboratory UPhoS (Ultrafast Photoemission Spectroscopy), GC acknowledges support from the Graphene Flagship (contract CNECT-ICT-604391). HH acknowledges financial support through the Postodctoral International Fellowship program of the Politecnico di Milano.

REFERENCES

Awschalom D D, L C Bassett, A S Dzurak, E L Hu, J R Petta (2013), "Quantum spintronics: Engineering and manipulating atom-like spins in semiconductors," *Science* vol.339, pp. 1174-9, doi: 10.1126/science.1231364

Beaurepaire E, J Merle, A Daunois, J Bigot (1996), "Ultrafast spin dynamics in ferromagneticnickel," *Phys,Rev,Lett,* vol.76,pp.4250, doi:10.1103/PhysRevLett.76.4250

Boschini F, H Hedayat, C Dallera, P Farinello, C Manzoni, A Magrez, H Berger, G Cerullo, E Carpene (2014), "An innovative yb-based ultrafast deep ultraviolet source for time-resolved photoemission experiments," *Rev,Sci,Instrum,* vol.85 , p. 123903, doi: 10.1063/1.4903347

Bugini D, F Boschini, H Hedayat, H Yi, C Chen, X Zhou, C Manzoni, C Dallera, G Cerullo, E Carpene (2017), "Ultrafast spin-polarized electron dynamics in the unoccupied topological surface state of Bi2Se3," *Journal of Physics: Condensed Matter*, vol.29 , pp. 30LT01, doi:

Cacho C, A Crepaldi, M Battiato, J Braun, F Cilento, M Zacchigna, M C Richter, O Heckmann, E Springate, Y Liu (2015), "Momentum-resolved spin dynamics of bulk and surface excited states in the topological insulator bi 2 se 3," *Phys,Rev,Lett*, vol.114 , pp. 097401, doi: 10.1103/PhysRevLett.114.097401

Carpene E, E Mancini, C Dallera, M Brenna, E Puppin, S De Silvestri (2008), "Dynamics of electron-magnon interaction and ultrafast demagnetization in thin iron films," *Physical Review B*, vol.78, pp. 174422, doi: 10.1103/PhysRevB.78.174422

Carpene E, E Mancini, C Dallera, G Ghiringhelli, C Manzoni, G Cerullo, S De Silvestri (2009), "A versatile apparatus for time-resolved photoemission spectroscopy via femtosecond pump-probe experiments," *Rev,Sci,Instrum*, vol.80 , pp. 055101, doi: 10.1063/1.3125049

Chen Y L, J Chu, J G Analytis, Z K Liu, K Igarashi, H Kuo, X L Qi, S Mo, R G Moore, D H Lu (2010), "Massive dirac fermion on the surface of a magnetically doped topological insulator," *Science*, vol.329, pp. 659-62, doi: 10.1126/science.1189924

Fan Y, P Upadhyaya, X Kou, M Lang, S Takei, Z Wang, J Tang, L He, M Montazeri, G Yu (2014), "Magnetization switching through giant spin-orbit torque in a magnetically doped topological insulator heterostructure," *Nature Materials*, vol.13, pp. 699, doi: 10.1038/nmat3973

Hajlaoui M, E Papalazarou, J Mauchain, G Lantz, N Moisan, D Boschetto, Z Jiang, I Miotkowski, Y P Chen, A Taleb-Ibrahimi (2012), "Ultrafast surface carrier dynamics in the topological insulator Bi2Te3," *Nano Letters*, vol.12, pp. 3532-6, doi: 10.1021/nl301035x

Hsieh D, F Mahmood, J W McIver, D R Gardner, Y S Lee, N Gedik (2011), "Selective probing of photoinduced charge and spin dynamics in the bulk and surface of a topological insulator," *Phys,Rev,Lett*, vol.107, pp.077401 ,doi: 10.1103/PhysRevLett.107.077401

Hsieh D, D Qian, L Wray, Y Xia, Y S Hor, R J Cava, M Z Hasan (2008), "A topological dirac insulator in a quantum spin hall phase," *Nature*, vol.452 , pp. 970-4, doi: 10.1038/nature06843

Hsieh D, Y Xia, L Wray, D Qian, A Pal, J H Dil, J Osterwalder, F Meier, G Bihlmayer, C L Kane (2009), "Observation of unconventional quantum spin textures in topological insulators," *Science*, vol.323, pp. 919-22, doi: 10.1126/science.1167733

Jozwiak C, J A Sobota, K Gotlieb, A F Kemper, C R Rotundu, R J Birgeneau, Z Hussain, D Lee, Z Shen, A Lanzara (2016), "Spin-polarized surface resonances accompanying topological surface state formation," *Nature Communications*, vol.7, p. 13143, doi: 10.1038/ncomms13143

Jung W, Y Kim, B Kim, Y Koh, C Kim, M Matsunami, S Kimura, M Arita, K Shimada, J H Han (2011), "Warping effects in the band and angular-momentum structures of the topological insulator bi 2 te 3," *Physical Review B*, vol.84, pp. 245435, doi: 10.1103/PhysRevB.84.245435

Kirilyuk A, A V Kimel, T Rasing (2010), "Ultrafast optical manipulation of magnetic order," *Reviews of Modern Physics* vol.82, pp. 2731.

Moore J E (2010), "The birth of topological insulators," *Nature* vol.464, pp. 194.

Ostler T A, J Barker, R Evans, R W Chantrell, U Atxitia, O Chubykalo-Fesenko, S El Moussaoui, L Le Guyader, E Mengotti, L J Heyderman (2012), "Ultrafast heating as a sufficient stimulus for magnetization reversal in a ferrimagnet," *Nature Communications* vol.3, pp. ncomms1666.

Park S R, J Han, C Kim, Y Y Koh, C Kim, H Lee, H J Choi, J H Han, K D Lee, N J Hur (2012), "Chiral orbital-angular momentum in the surface states of bi 2 se 3," *Phys,Rev,Lett*, vol.108 , pp. 046805.

Roushan P, J Seo, C V Parker, Y S Hor, D Hsieh, D Qian, A Richardella, M Z Hasan, R J Cava, A Yazdani (2009), "Topological surface states protected from backscattering by chiral spin texture," *arXiv Preprint arXiv:0908.1247*.

Snchez-Barriga J, M Battiato, M Krivenkov, E Golias, A Varykhalov, A Romualdi, L V Yashina, J Minr, O Kornilov, H Ebert (2017), "Subpicosecond spin dynamics of excited states in the topological insulator bi 2 te 3," *Physical Review B* vol.95 , pp. 125405.

Sobota J A, S Yang, J G Analytis, Y L Chen, I R Fisher, P S Kirchmann, Z Shen (2012), "Ultrafast optical excitation of a persistent surface-state population in the topological insulator bi 2 se 3," *Phys,Rev,Lett*, vol.108 , p. 117403, doi: 10.1103/PhysRevLett.108.117403

Wang Y H, D Hsieh, D Pilon, L Fu, D R Gardner, Y S Lee, N Gedik (2011), "Observation of a warped helical spin texture in bi 2 se 3 from circular dichroism angle-resolved photoemission spectroscopy," *Phys,Rev,Lett*, vol.107 , p. 207602, doi: 10.1103/PhysRevLett.107.207602

Wolf S A, D D Awschalom, R A Buhrman, J M Daughton, S Von Molnar, M L Roukes, A Y Chtchelkanova, D M Treger (2001), "Spintronics: A spin-based electronics vision for the future," *Science* vol.294, pp. 1488-95, doi: 10.1126/science.1065389

Wray L A, S Xu, Y Xia, D Hsieh, A V Fedorov, H Lin, A Bansil, Y S Hor, R J Cava, M Z Hasan (2011), "A topological insulator surface under strong coulomb, magnetic and disorder perturbations," *Nature Physics* vol.7, pp. 32-7, doi: 10.1038/nphys1838

Zhang T, P Cheng, X Chen, J Jia, X Ma, K He, L Wang, H Zhang, X Dai, Z Fang (2009), "Experimental demonstration of topological surface states protected by time-reversal symmetry," *Phys,Rev,Lett*, vol.103 , pp. 266803, doi: 10.1103/PhysRevLett.103.266803

Zhu Z, G Levy, B Ludbrook, C N Veenstra, J A Rosen, R Comin, D Wong, P Dosanjh, A Ubaldini, P Syers (2011), "Rashba spin-splitting control at the surface of the topological insulator bi 2 se 3," *Phys,Rev,Lett*, vol.107 , pp. 186405, doi: 10.1103/PhysRevLett.107.186405