ISpinText - Induced Spin Textures in van der Waals Heterostructures

I. Introduction

After the discovery of graphene it was soon realized, that graphene is the perfect candidate for spintronics, due to its high mobility, low spin-orbit coupling and small or absent hyperfine fields. By now, spin relaxation lengths longer than 10 um have been demonstrated, which makes graphene an ideal platform to transfer spin information. The key question at the present stage, how the manipulation of spin can be achieved with graphene devices. We investigated novel routes to add electric and magnetic control over the spin by introducing different spin textures in graphene. Spin textures are induced by developing various 2D proximity heterostructures, e.g. when graphene is combined by other 2D materials. These materials include transition metal dichalcogenids, and novel materials, with huge spin-orbit coupling, like BiTeI. The induced SOI can enable control of the spin-direction. The presence of SOI is tested by weak localization, non-local spin injection measurements or spin-Hall measurements.

II. Results

II.1 Exfoliation of single layer BiTeI

In order to produce heterostructures with huge spin-orbit materials, first we investigated the fabrication of nanocrystals of BiTeI with the standard cleaving process with adhesive tape and characterized their surface properties optically and by AFM etc [d1]. We also investigated different contacting materials to create nanoelectronic devices out of them to address mobility, carrier density and study the effect of gating. The cleaving process works, however the size of the crystals are very small (~um^2) and to reach thickness bellow 10-20nm is challenging with BiTeI.

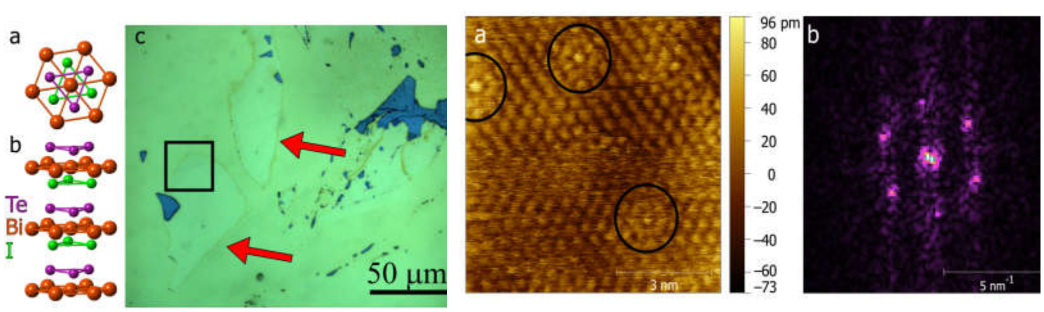


Fig. 1 Exfoliation of single layer BiTeI *(Left panel): BiTeI combines structural inversion anisotropy and the presence of Bi as a heavy element, which results in a giant spin-orbit interaction in bulk form. Using a special exfoliation technique based on attaching the bulk crystal to strip gold surface and removing it by ultasonication, single layer BiTeI remains on the gold surface. As subpanel c shows the position of the single layer BiTeI can be identified by optical microscope images. (Right panel): High resolution STM image at the BiTeI monolayer surface (a), which shows the lattice periodicity related to BiTeI crystal structure also at the FFT of the STM image (b). [1]*

In order to overcome this problem, in collaboration with group of L. Tapaszto (MFA), we developed special exfoliation technique of BiTeI, which resulted single layer BiTeI for the first time [3]. The technique relies on the strong adhesive interaction between freshly stripped gold surface and BITeI. Based on the calculation of our colleagues from ELTE (Z. Tajkov, L. Oroszlany, J. Koltai) this interaction is even stronger that the binding energy between BiTeI monolayers, therefore the sonication of the gold/BiTeI bulk stack results a monolayer of BiTeI on the gold surface. With detailed optical microscopy, STM and AFM studies we could proof experimentally the existence of monolayer BiTeI on the gold surface. Flakes with remarkable large size of 100um and good stability (longer than one month) were demonstrated. [1]

II.2 Dry Stacking setup to realize heterostructures

To fabricate heterostructures, with graphene and huge spin-orbit materials or other magnetic compounds (e.g. magnetic insulators), we develop a dry stacking setup where the combination of pdms/ppc used as a transparent substrate to transfer various layers. The setup allows fine positioning of the layers with optical microscope using magnification of x500 and x1000 and micromanipulators. It has a stage with heater and a motor controlled z axis motion which allows to release the layers in a controllable way. First we optimized the setup with fabrication of hBN/graphene stacks, which were successfully produced. As a next step BiTeI crystals were also introduced into the stacking process and successfully combined with graphene [d1].

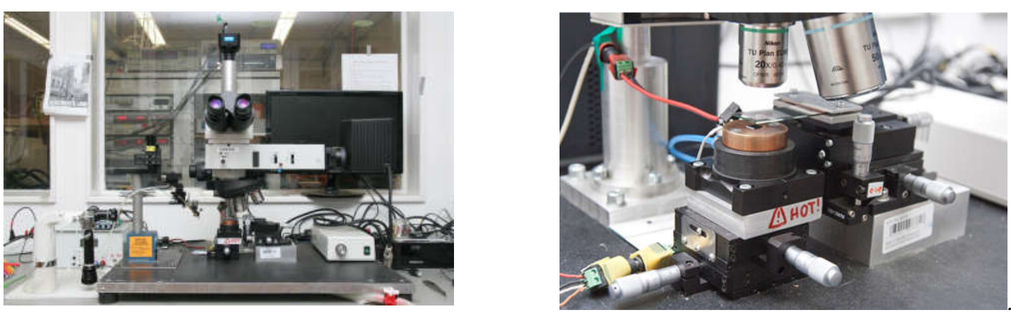


Fig. 2 Stacking setup *(Left) Optical microscope which allows the visual contron on the stacking process. (Right) Stage with micromanipulators, where different 2D layers from pdms/ppc mask can be positiioned and released by local heating.*

II.3 Tuning the Rashba parameter in BiTeBr by ionic liquid gating [8]

In addition, we also started exfoliation of another potentially 2D candidate crystal: BiTeBr. After first tests with conventional exfoliation techniques it seems that achieving thin structures is much more promising than for BiTeI. Since BiTeBr and BiTeI have the same crystal structure and SOI is also strong for BiTeBr, it is an other candidate for proximity SOI layer. Furthermore BiTeBr has another attractive property that the size of polar domains is above 1µm, while for BiTeI is in the range of 50nm.

Thus in a nanocircuit based on BiTeBr the built-in E field does not change sign. Due to these superior properties we used BiTeBr for our further studies. We managed to exfoliate BiTeBr down to thickness of 20nm with standard adhesive tape based exfoliation procedure. In BiTeBr or BiTeI crystals there is a finite electron density in the conduction band ($1e^{-18}$ - 1^{-19} cm^{-3}). In order to enhance the role of the Rashba spin-orbit interaction it is desired to bring the chemical potential closer to the bottom of the conduction band (See Fig. 3). When a flake is sufficiently thin with electric gating the density of the crystal can be changed. In BiTeBr the thin flakes already allowed to change the electron density, however the variation was small, only <1%. To enhance the density variation we started to work with ionic liquid gating technique in collaboration with Justin Ye (Univ Groningen). Unfortunately ionic liquid induced chemical interaction with BiTeBr, therefore advanced sample fabrication was required, which includes thin (3-5nm thick) hBN cover layer to protect BiTeBr [d8]. Schematics of the final setup is shown in Fig. 3 middle panel. Due to the giant Rashba spin-orbit term, BiTeBr expected to show peculiar transport behavior. The resistance is non-reciprocal in finite B field, i.e. for changing the sign of the current, resistance changes: R(I)<>R(-I). Our measurements confirmed this prediction. Furthermore the strength of the non-reciprocal behavior is expected to increase as the electron density is decreased. With ionic gating we could demonstrate this effect as Fig. 3 shows. The experimental variation of the non-reciprocal signal was significantly larger than expected from theory [8].

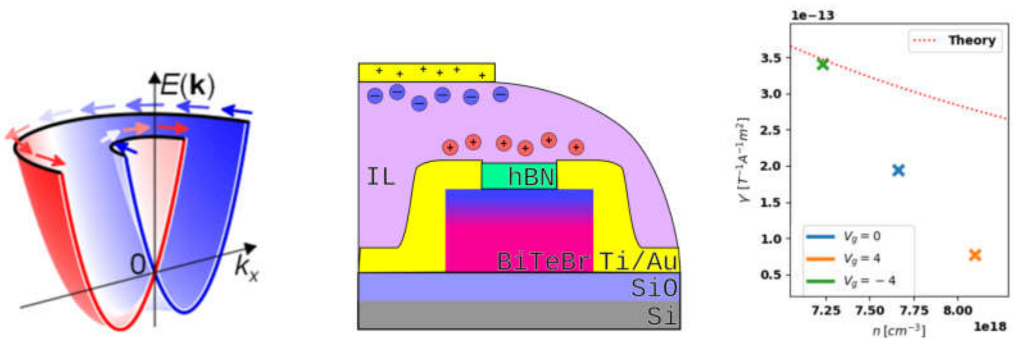


Fig. 3 Ionic gating of BiTeBr *(Left) Dispersion relation of Rashba spin-orbit interaction of BiTeBr. Arrows show the spin orientation of states. (Middle) Ionic gating setup: BiTeBr is covered by 3-5nm hBN layer to protect it from chemical interaction with ionic liquid. Potential applied to upper electrode, which separate the ions in the liquid (IL) and results large positive/negative charge accumulation on hBN surface, which increases/decreases electron density in BiTeBr. (Right) Strong enhancement of the non-reciprocal response of BiTeBr as the electron density is reduced by ionic gating. V_g is voltage applied on ionic liquid. [8]*

II.4 Fabrication of BiTeX/graphene heterostructures and WL measurements

As thin layers of BiTeBr and BiTeI were produced, the development of graphene BiTeX (X=Br or I) heterostructure was the next step [d4]. Our goal was to place a BiTeBr crystal on top of graphene sample and study the proximity induced spin-orbit interaction first by weak antilocalization (WAL) measurements. Typical device geometry is shown in Fig. 4 Left panel. Carrying out 4K magnetotransport measurements only weak localization (WL) signal was measured, the averaged conductance increased with magnetic field. In case of sufficient spin-orbit interaction the magnetic field dependence should be opposite, which is called antilocalization signal.

To understand better the heterostructure we carried out systematic characterization steps. We investigated the cleaved BiTeBr flakes by AFM, Raman and EDS measurements (thanks to S. Lenk, P. Kun, L. Illes). It turned out that thinnest flake (<30nm, with optical color different from yellow) cleaved from the growth crystal are not BiTeBr. As the Raman and EDS spectra identified they are BiOBr insulator layers. With further checks we proved that oxidation does not take place after exfoliation but these BiOBr pieces are part of the growth crystal.

Furthermore we realized that the surface of BiTeBr after exfoliation process is not as clean as that of graphene. Contaminants from the adhesive tape remains on the surface. To overcome that a) special exfoliation technique was applied, which take place in a fridge at temperature of 3-4C or b) heat treatment is used to remove the contamination by annealing at 350C at vacuum.

AFM studies pointed out that the surface of BiTeBr cleaves not as perfectly as graphene or other TMDCs, several terraces form with few nm heights, which could also prevent to make a good interface with graphene [d1].

In addition BiTeX are polar materials which attracts charged contaminants to link to the surface, thus a perfect fresh BiTeBr surface could also get contamination at ambient condition. To analyze whether this generates a lake of induces spin-orbit interaction we also built graphene/BiTeBr heterostructures in glovebox system in argon atmosphere. Since stacking microscope was not available inside, device fabrication required different technique. From CVD graphene thin graphene stirpes were fabricated on a silicon substrate, then BiTeBr was pressed to the substrate and BiTeBr crystals landed randomly on the surface. WL measurements on these devises showed again no signature of spin-orbit effect. One also cannot exclude that contamination could added to the interface after creation of the heterostructure during lithography process. To avoid this case additional hBN procetting layer was also added from the top to encapsulate the heterostructure [d4]. However it also did not induced visible spin-orbit proximity by WAL.

In case of weak proximity spin-orbit interaction WAL signal is only visible at very low temperatures T<1K. To check this possibility, we carried out WL measurements in the probe of our dry dilution refrigerator. It turned out that standard chip carrier setup and wiring does not allow such a measurement, since only extreme slow magnetic field ramp rate (<1mT/min!) was allowed without heating of the sample older. By systematic study we identified that also all elements of our standard cold head like standard PCB, Socket, Filters, soldering all contributes to heating. By eliminating them we realized a cold head where ramp rate of 35mT/min is achievable at temperature of 60mK. Detailed WL measurements at this conditions also did not show signature of spin-orbit interaction (see Fig. 4 Right panel).

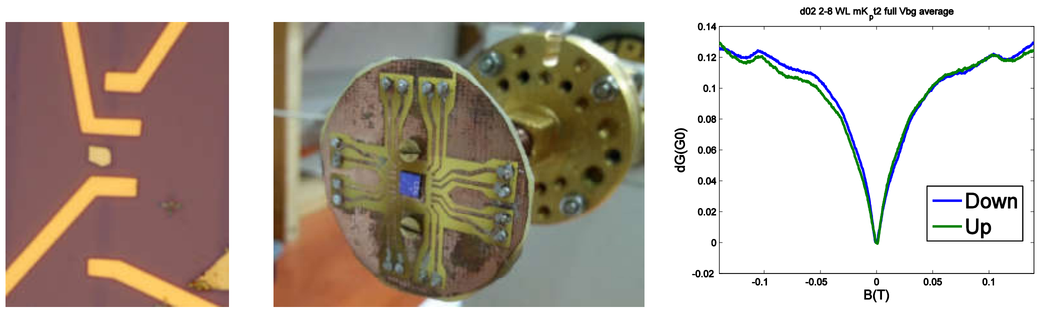


Fig. 4 Weak Localization measurements on BiTeBr/graphene heterostructure *(Left) CVD device geometry. On a CVD graphene (vertical blue stripe in the middle) 4 electrodes are fabricated (yellow) and a BiTeBr flake is deposited between the two middle electrodes on graphene (dark yellow). The width of electrical contacts is 300nm. (Middle) New cold head of dilution fridge sample holder, where indium soldering, Cu/epoxy PCB is used, no chip socket and carrier to reduce eddy current heating. (Right) Weak localization measurement at 60mK on BiTeBr/graphene heterostructure. Signal is averaged in a several volts wide gate voltage range. Conductance increases with B field, which means weak localization signal, i.e. absence of signature of spin-orbit proximity. [d2]*

II.5 Spin-orbit coupling in graphene/WSe heterostructures

To generate proximity induced spin-orbit interaction, we also developed and investigated other heterostructures (in col. with group of C. Schonenberger, UBasel) [d6]. Grapehene was combined with WSe layer and capped with insulator hBN for surface protection (see Fig. 5 top panels). Indeed the interaction with this TMDC material resulted a proximity spin-orbit interaction in graphene. Weak localization measurements showed anti-localization signal (see Fig. 5 lower panels). Careful analysis was carried out to identify the nature of spin-orbit term in graphene. The weak localization signal was studied as a function of electron density and magnetic field orientation. Based on the analysis it was concluded that the spin relaxation of the in-plane spins is largely dominated by a valley-Zeeman spin-orbit coupling and that the intrinsic spin-orbit coupling plays a minor role in spin relaxation. [4].

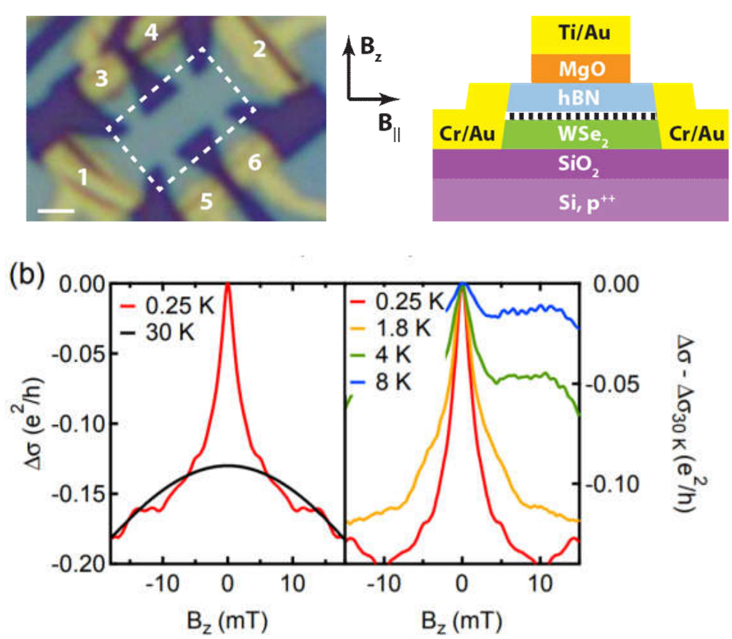


Fig. 5 Weak anti-localization of graphene/WSe *(Up) Device geometry: graphene is encapsulated between WSe_2 and hBN, which results high mobility.(Down) Resistance as a function of external perpendicular magnetic field averaged in a gate voltage window. At low temperatures the resistance shows a peak at B_z=0, which is resulted by weak antilocalization effect. It is a signature of proximity spin-orbit interaction.*

II.6 Confinements in graphene

For spintronics devices conductance channels which are not influenced by the edge disorder of the graphene flake are promising. We have demonstrated such channels along the interfaces of differently doped region of graphene flake. P-N junctions were created along the longitudinal direction of the sample, its interface serves as a conductance channel in the bulk of the graphene flake. [3]

Confinement of individual electrons in quantum dots is a promising way to represent quantum information with spin of electron. Electrostatic formation of quantum dots is challenging in graphene due to the gapless spectrum. We demonstrated a novel way around this problem, by using the Landau-gap in magnetic field to realize smooth confinement potential of quantum dots. [2,d3]

II.7 Influence of strain on BiTeX/graphene heterostructures

Heterostructure of graphene and BiTeX is also encouraging to create exotic electronic structures. In collaboration with colleagues from ELTE (J. Koltai and L. Oroszlany) we showed that graphene/BiTeX heterostructures under mechanical strain could go through a phase transition (see Fig. 6) and it could become a time reversal invariant topological insulator. Based on first principle DFT calculations an effective tight binding model was introduced to handle the electric structure of BiTeX-graphene system. [6] The effect of in-plane uniaxial strain and stress perpendicular to the device were investigated. Out-of plane strain widens the initially present trivial band gap of BiTeBr, while in-plane strain drives the system into the topological phase. In plane strain could be generated by structural stress inherently present in heterostructures placed on substrate [7].

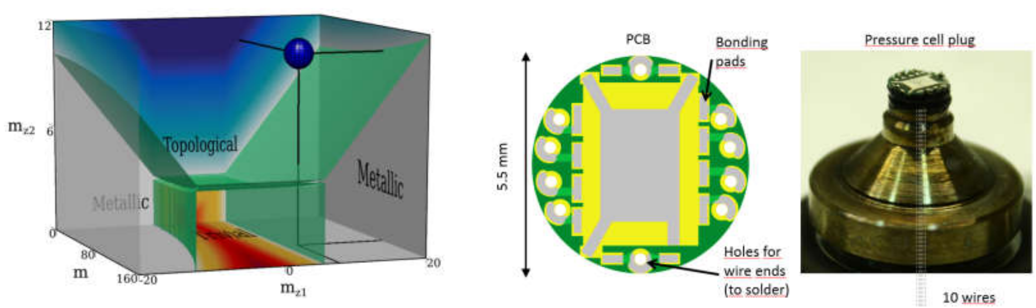
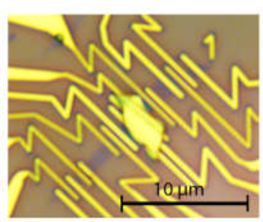


Fig. 6 Heterostructures under strain *(Left)Topological phase diagram of graphene/BiTeBr structure. The electron structure of the system shows a reach phase diagram as in-plane uniaxial strain or out-of plan stress is applied.[6] (Right) Parts of the developed pressure cell, which allows to study nanocircuits under pressure. Small PCBoard is integrated on the plug of the cell, which hosts the silicon chips.[d7]*

In order to be able to study heterostructures under strain we have also developed a new measurement setup, which allows to investigate nanocircuits under pressure [d7]. We built a dedicated pressure cell plug containing a PCB with bonding pads, which hosts the silicon wafer of the nanocircuits in the cell (see Fig. 6). The nanocircuits are surrounded by kerosene, which transfers the pressure applied from outside. We showed that an additional hBN cover layer on the circuits prevent the interaction with the pressure transmitting liquid and there is no significant mobility reduction due to kerosene. Measurements up to 25kbar were carried out on first test samples, which contained two graphene layer stacked on top of each other with hBN cover layer.

II.8 Non-local spin transport measurements on BiTeBr/graphene heterostructures

The absence of weak antilocalization signal does not mean the absence of proximity spin-orbit interaction, since for certain type of spin-orbit coupling does not generate weak antilocalization signal. Thus we also investigated the influence of BiTeBr on the spin property of underlying graphene by spin valve measurements (see Fig. 7). BiTeBr crystal was placed on a graphene flake and several ferromagnetic Co/TiOx electrodes were defined around it. By injecting current from a ferromagnetic electrode spin polarization is generated in the graphene flake which diffuses away. With additional ferromagnetic detectors the spin polarization is detected on the other side of the BiTeBr flake. In case of proximity spin-orbit interaction the spin diffusion length under the BiTeBr flake should decrease compare to case of pristine graphene. The spin diffusion length was determined by Hanle measurements and no significant difference between a bare graphene and graphene/BiTeBr channel was observed. They both had spin diffusion length of τ_S=150±40ps. To understand better the influence of BiTeBr contact were added on top of the BiTeBr flake as well (see Fig 7, right lower panel). Transport measurements through the graphene/BiTeBr interface showed that the interface resistance is large (R_i > 30kΩ), which could reduce the desired proximity spin-orbit effect.



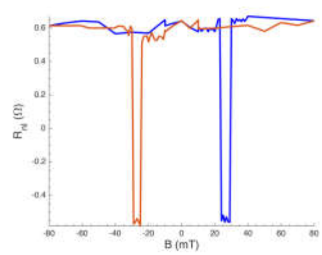
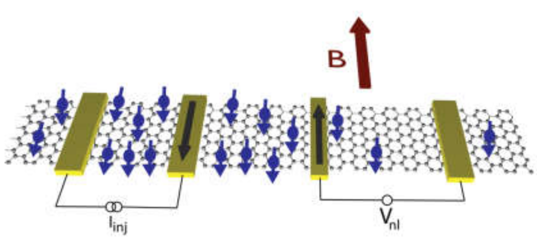
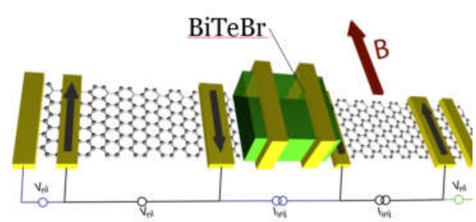


Fig. 7 Non-local spin valve measurements on graphene BiTeBr heterostructure *(Left) Optical image of a spin valve device. Light blue is the graphene flake, yellow object in the middle is BiTeBr crystal and yellow electrodes are ferromagnetic Co leads with TiOx tunnel barrier [d5]. (Right) Non-local spin valve signal as a function of external B field applied parallel to Co electrodes.*





(Left Up) Schematics of non-local spin valve measurement. Current (I_{inj}) flows between two right leads. It injects spin polarized electrons from the ferromagnetic lead (second left one). Injected spin polarized electrons diffuse towards the two right electrodes used to measure voltage. Since chemical potential of spin up/down electrons is different, non-local voltage (V_{nl}) is measured with the ferromagnetic detector electrodes. (Right Up) Spin valve geometry with a BiTeBr crystal (green) in the middle segment. Two top contacts are added on top of BiTeBr flake [d5].

II.9 Electric controlled spin injection from BiTeBr to graphene

The large resistance at the graphene/BiTeBr interface allows to use the BiTeBr as an injector avoiding conductance mismatch due to the large difference in electron density of the two layers. Thus we carried out measurements when electrons are injected from BiTeBr towards graphene (see Fig. 8). The current was drained to one side of the BiTeBr crystal while the spin population was detected by non-local voltage measurement on the other side of the crystal. Surprisingly a robust non-local voltage was measured, which depends on the polarization of the detector electrode. The non-local signal changes sign if the direction of the electron current is changed. The non-local signal was detected on the other side of the BiTeBr crystal as well. The non-local signal shows Hanle like characteristics in perpendicular magnetic field. These features provide a clear evidence that spin injections take place as current flows from BiTeBr to graphene[7]. Since BiTeBr has no net spin polarization, additional process is required to explain these experiments. Indeed the giant Rashba spin-orbit interaction of BiTeBr could generate the observed spin injection. Since the main free path in BiTeBr is short, several scattering events take place in the crystal which in the presence of strong spin-orbit interaction generates Spin Hall Effect (SHE). SHE results spin polarized electrons at the surface of the crystal, which then injected to the graphene. Another explanation is based on Rashba-Edelstain Effect, where the Rashba dispersion relation generates spin polarization in the presence of electric field.

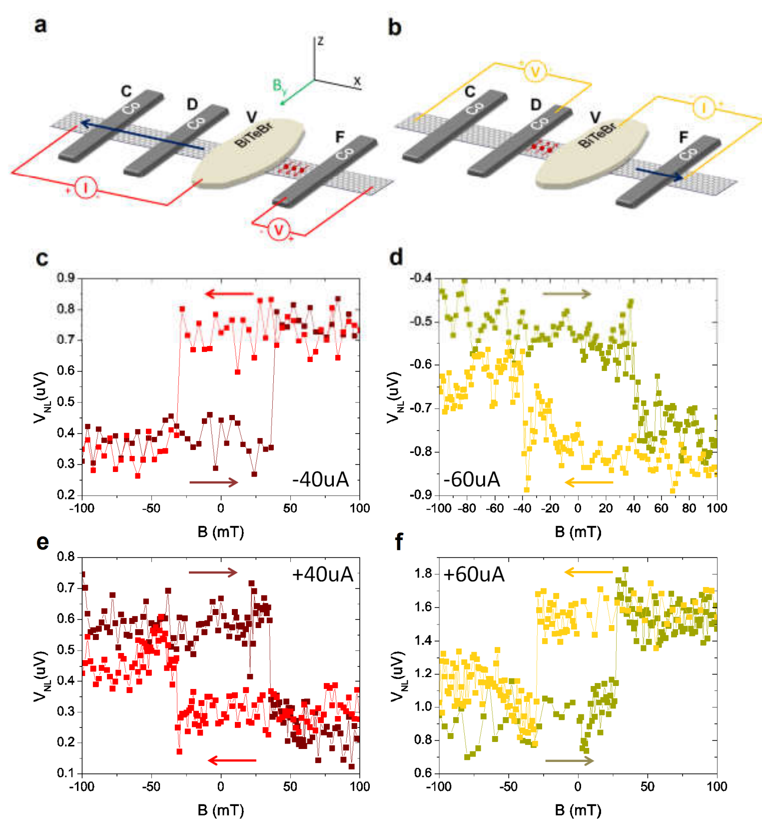


Fig. 8 Non-local detection of spin injection from BiTeBr to graphene *Panel a and b represent the measurement setup, measuring nonlocal voltage at FM contacts F and D, on opposite sides of the BiTeBr flake (contact V). The magnetic field is applied along the FM contact easy axis. The dark blue arrows represent the charge current during the measurements in c and d, and are opposite for e and f. Panels c and e show the detected nonlocal signal on FM contact F, using both positive and negative bias current, respectively. Panels d and f show the same for detected nonlocal signal on FM contact D.* [7]

In summary, our final goal to engineer spintronic functionality into BiTeX/graphene heterostructure was achieved. The above described novel effect allows to use graphene/BiTeBr as a spin injector, where the spin polarization can be simple controlled by electric signal.

III. Added values of the project

In addition to the published scientific results and the developed new infrastructure (like stacking setup, low T WL sample holder, pressure cell), the present project allowed dedicated spintronics training for young scientists and students. During the three-years of the project, 1 phd and 3 diploma students spent more than 7 months in leading laboratories of the field of spintronics at University of Basel, University of Groningen or Chalmers University and learnt special techniques (ionic-gating, high quality stacking, non-local spin valve measurement) and transferred the know-how to Budapest. Last but not least, the project provided the necessary background to write 4 BSc thesis, and additional 3 MSc thesis and 1 phd thesis will also be written. Furthermore the project also resulted 4 TDK works, which received the prestigious 1st and 3rd prize in local TDK and also on OTDK together with additional special prizes.

IV. Publications

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[d5] B. Szentpéteri, TDK Dolgozat, Nem-lokális spintranszport mérések grafén/BiTeBr heteroszerkezetekben (2018)

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