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Spin-resolved electronic dynamics in bulk WSe_2

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Introduction

Transition metal dichalcogenides MX_2 (TMDC) are 2D-like Van der Waals layered materials with peculiar properties ranging from superconducting physics to strong light-matter interactions. Within this wide family of materials, the semiconducting (Mo and W as metal and S, Se and Te as chalcogenide) class possesses remarkable optical and electronic properties which has triggered a huge amount of interest in recent years. The nature of bonding in these materials allows isolated monolayers to be produced, in a way similar to graphene. Due to the lack of inversion symmetry and strong quantum confinement in monolayers, at the atomic thickness limit these materials possess exotic quasiparticles (exciton, trions, etc) with large binding energy. Furthermore, they are semiconductors with a direct band gap located at the boundary of the Brillouin zone (BZ) in the K valley and at this position a correlation between spin and valley degree of freedom is formed [1,2]. Indeed, by excitation with circular polarized light it is possible to populate one of the two inequivalent subsets of K valleys (referred to as K or K'). In the 2H-bulk phase, these materials lose the direct band gap character and the inversion symmetry is restored by stacking layers with opposite orientation.

However, it was recently proposed [3] and later demonstrated that bulk TMDCs could host purely spin polarized valence bands despite being inversion symmetric [4]. This is due to the combined effect of local atomic site asymmetry and large spin orbit coupling generated by heavy atomic elements. Thanks to these features, it is possible to generate spin and valley polarized carriers by means of circular light photo-excitation as previously demonstrated [5]. So far, the direct access to the spin polarization of the excited carriers is lacking. It remains a technological challenge to perform such experiment in the time domain due to the very low figure of merit of spin-resolved photoelectron detection. Here, we want to take advantage of the highly localized character of the excited states in the K valley just after photo-excitation.

Spin- and valley-selective excitation

Bulk 2H-WSe_2 is an indirect semiconductor with a bandgap of around 1.2 eV. In the 2H-polytytpe, it has a hexagonal symmetry with a unit cell based on two adjacent atomic layers flipped by 180° with respect to each other. The maximum of the conduction band is located at the center of the BZ in the Γ point but almost degenerated with the BZ corners where the K points lie (see Fig. 1). At these points, the valence band is split due to spin-orbit coupling with an energy splitting of almost 0.5 eV. The gap at the boundary of the Brillouin zone has a direct character allowing for an optical excitation at an energy of around 1.6 eV. At these K points, the conduction band presents a local minimum, which we refer to as the K valley for the photo-excited carriers. According to both theory and experiment [4], the dispersion of electronic states at the K point is nearly flat in both valence and conduction bands indicating a strongly bi-dimensional character of these states. So to first approximation, states at the K point are confined within a single atomic layer partially restoring the monolayer physics.

Bulk WSe_2 crystals were cleaved in ultra-high vacuum. The material is probed with a 21 eV XUV light pulse produced by High Harmonic Generation at the Artemis end station. This photon energy ensures a mean free path close to the single atomic layer thickness [4,5]. By doing so, we can probe the asymmetric part of the unit cell allowing access to both spin and valley degrees of freedom despite working with bulk material. The material is pumped with 1.6 eV light pulses with circular polarization. This pump energy matches the direct bandgap and creates a well-defined electron population in the K valley with a well-defined spin and valley polarization. The overall time resolution of the experiment is about one hundred femtoseconds.

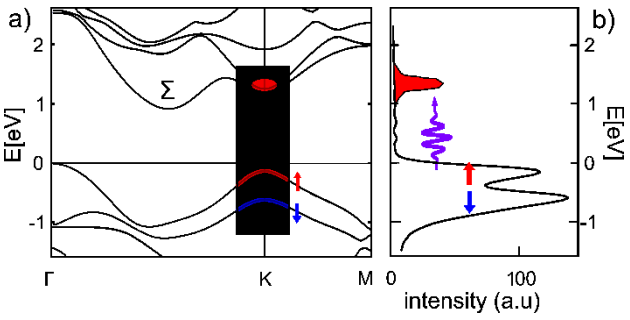

Figure 1 A) *Schematic representation, based on DFT calculations, of the band structure of the WSe_2 along the M-K-Γ axis. At the K point the two valence bands are purely spin polarized (red and blue arrows). The grey shaded area corresponds to the probed area with the spin-resolved detector.* ***B)*** *Projection onto the energy axis of the valence band at the K point. The arrows depict the expected spin polarization of electrons. The red area denotes the excited state into the K valley after direct photo-excitation.*

The detection is done through time-of-flight technique allowing for good energy resolution but at the cost of the angular momentum information. Despite this fact, as the angular aperture is small, it is still possible to map a well-defined part of the reciprocal space. The spin-resolved detection is perform by using a Mott detector but this detection does not provide a

direct access to the spin polarization. Instead, the detector records 4 channels corresponding to the projection of four spin components (horizontal up and down, vertical up and down) (see Fig. 2) but the efficiency is this scattering process with respect to the spin polarization is not unity.

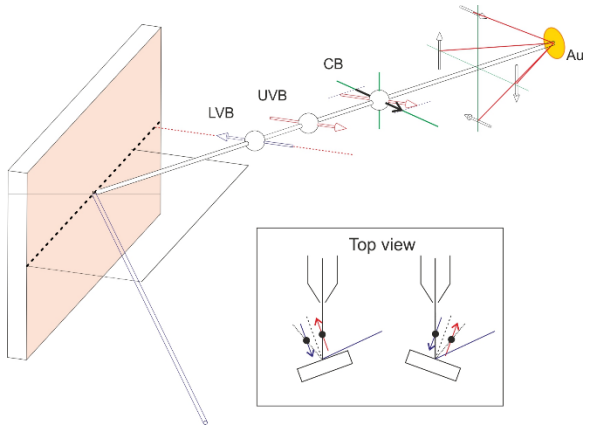

Figure 2 *Scheme of the spin-resolved detection with the experimental geometry. Valence bands purely spin polarized along the z-axis should translate into spin-polarized signal along the horizontal axis of the detector.*

By consequence, in spin-resolved detection mode, one has first to calibrate the response function of the detector. The most common way is to use magnetic sample with easy magnetic reversal such as ferromagnet like Ni or Fe. The procedure is to measure the photoelectron spectra for opposite spin-orientation thus providing the response function of the detector. In our case, the material is non-magnetic but it is still possible to find purely spin-polarized electrons. Indeed, by looking at the valence bands of the K point one expects at certain photon energies to have purely spin polarized bands with opposite spin polarization. We calibrate the detector by measuring photoelectron produced by the support in cooper. This signal is supposed to be non-magnetic and we correct the channels response with that respect.

Spin-resolved excited carrier dynamics

The photo-excitation with circular polarized light at 1.6eV photon energy results in spin and valley polarized electron gas in the K valleys of bulk WSe_2. Afterwards, electrons scatter within few hundreds of femtoseconds towards the global minimum of the conduction band in the Σ valley (see Fig. 1) [5]. Regarding the valence bands, with the proper detector calibration, we are able to retrieve the purely spin-polarized character of the valence bands thus confirming previous experimental observation [4].

We chose to investigate the spin polarization of excited carrier directly at time zero where the signal is at a maximum in the K valleys. The signal obtained in the conduction band reveals a clear spin polarization of the excited electrons (see Fig. 3). This net spin polarization matches the polarization of the top valence bands at this inequivalent K valley. It implies that such spin- and valley-polarized carriers appears instantaneously in the three inequivalent K valleys of the probed topmost layer. In addition, due to the low dimensionality of the electronic state in K valley, it results in the creation of purely spin polarized electron gas within each layer of the bulk material. This represent the first direct observation of the spin polarization of excited carriers in a semiconductor TMDC.

A key question is the evolution of the net spin polarization of the electron gas upon scattering towards the Σ valley. Since these electronic states are three dimensional, it is vital to know if the polarization is maintained and for how long in order to harvest this initial spin- and valley-polarized carrier.

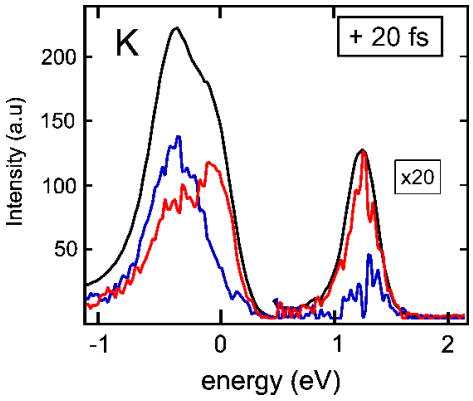

Figure 3 *Spin-resolved photo-electron spectra of WSe_2 around the K valley. The black line corresponds to the photoelectron signal without spin discrimination. The spin polarized valence bands are discriminated through the spin resolution. The red trace corresponds to horizontal up with respect to the detector geometry. The blue trace corresponds to horizontal down with respect to the detector geometry. The excitation with circular light polarization results in net spin-polarization of photo-carriers in the K valleys expressed by the clear spin up majority of the excited carriers in the K valley.*

From a technical point of view, due to the low efficiency of the Mott detector, the acquisition of such spectrum takes about 12 hours in order to get decent statistics in the excited state. It renders the complete evolution in the time domain of such spin polarization virtually impossible with the current setup.

Conclusions

By taking advantage of circularly polarized pump and high harmonic XUV pulses provided by the Artemis facility to perform time- and spin-resolved photoemission, we have directly observed the generation of carriers with a defined spin and valley momentum in bulk WSe_2. It emphasizes that it is now possible to investigate in the time domain the evolution of the spin polarization of electrons following an ultrafast photo-excitation. The evolution of such initially spin polarized electron population within the Brillouin Zone represents the next challenge. The development of new spin-resolved detector with better figure of merit together with the improvement of the Artemis end station, especially the increase of repetition rate, should strongly improve the feasibility of this kind of experiment in the future.

Acknowledgements

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