Exciton dynamics in WSe$_2$ bilayers

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We investigate exciton dynamics in 2H-WSe$_2$ bilayers in time-resolved photoluminescence (PL) spectroscopy. Fast PL emission times are recorded for both the direct exciton with $\tau_D \lesssim 3$ ps and the indirect optical transition with $\tau_I \approx 25$ ps. For temperatures between 4 to 150 K $\tau_I$ remains constant. Following polarized laser excitation, we observe for the direct exciton transition at the $K$ point of the Brillouin zone efficient optical orientation and alignment during the short emission time $\tau_D$. The evolution of the direct exciton polarization and intensity as a function of excitation laser energy is monitored in PL excitation (PLE) experiments.

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Thin layers of transition metal dichalcogenides (TMDCs), such as MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$ have emerged as very promising materials for optical, electronic and quantum manipulation applications [1, 2]. The opto-electronic and spin properties in TMDCs can be controlled at an atomic layer level: In TMDC mono-layers (MLs), the lowest energy inter-band transition at typically 1.8 eV is direct in k-space [3, 4] with strong optical absorption ($\approx 10\%$). In MLs crystal inversion symmetry breaking together with the strong spin-orbit (SO) interaction leads to a coupling of carrier spin and k-space valley physics, i.e., the circular polarization ($\sigma^+$ or $\sigma^-$) of the absorbed or emitted photon can be directly associated with selective carrier excitation in one of the two non-equivalent $K$ valleys ($K^+$ or $K^-$, respectively) [5, 11]. Moreover, the strong Coulomb interaction between electrons and holes results in large exciton binding energies of typically 500 meV as recently predicted [12, 13] and experimentally confirmed [14, 18].

The physical properties drastically change when going from a ML to bilayers: First, in TMDC bilayers the lowest energy optical transition is indirect in k-space, similar to the bulk material [3, 4, 19, 20]. Time-integrated photoluminescence (PL) spectroscopy reveals in addition a higher energy direct transition associated to the recombination of carriers at the $K$ point. Second, crystal inversion symmetry is recovered in TMDC bilayers (the upper layer is rotated by 180° with respect to the lower one in 2H-WSe$_2$). As a result the chiral optical valley selectivity important for MLs should vanish, and no spin splitting in the bands is expected. Surprisingly, following polarized laser excitation, strongly polarized PL emission of the direct transition have been reported in time-integrated experiments recently in bilayer WSe$_2$ [21] and WS$_2$ [22]. As possible origins, theoretical calculations suggest (i) intrinsic circular polarization in centrosymmetric even-layer stacks of TD MCS [21, 23] and (ii) the excimer effect [24].

To shed light on the competition between direct and indirect optical transitions and the intriguing spin and valley physics, we perform time- and polarization resolved PL experiments as a function of temperature and laser excitation energy. In contrast to MLs, where the carrier dynamics has been measured by time-resolved absorption, reflection or PL spectroscopy [25, 29], the measurement of both the direct and indirect optical transition kinetics have not been reported in TMDC bilayers to the best of our knowledge. We show that the direct transition in the bilayer is characterized by a very short decay time $\tau_D \lesssim 3$ ps at low temperature, similarly to WSe$_2$ MLs [30]. The exciton dynamics of the indirect transition is about ten times longer with a decay time of $\tau_I \approx 25$ ps, with a weak temperature dependence. Moreover we demonstrate that the exciton (pseudo-)spin...
polarization and coherence measured on the direct optical transition occur on a very short time-scale of a few picoseconds. These results are also interesting in the context of TMDC heterostructures, proposed recently for photovoltaic or water-splitting applications where the knowledge of the electronic excitations dynamics is essential [31,32].

Experimental set-up and sample.— WSe$_2$ flakes are obtained by micro-mechanical cleavage of a bulk WSe$_2$ crystal (from 2D Semiconductors, USA) on 90 nm SiO$_2$ on a Si substrate. The bilayer region is identified by optical contrast (see inset of Fig. 1a) and very clearly in PL spectroscopy. Experiments between T=4 and 300 K are carried out in a confocal microscope optimized for polarized PL experiments [33]. The WSe$_2$ bilayer is excited by picosecond pulses generated by a tunable frequency-doubled optical parametric oscillator (OPO) synchronously pumped by a mode-locked Ti:Sa laser. The typical pulse and spectral width are 1.6 ps and 3 meV respectively; the repetition rate is 80 MHz. The laser average power is in the 200 µW range, in the linear absorption regime. The detection spot diameter is ≈1 µm. For time integrated experiments, the PL emission is dispersed in a spectrometer and detected with a Si-CCD camera. For time-resolved experiments, the PL signal is dispersed by an imaging spectrometer and detected by a synchro-scan Hamamatsu Streak Camera with an overall time resolution of 3 ps. The circular PL polarization $P_c$ is defined as $P_c = (I_{\sigma+} - I_{\sigma-})/(I_{\sigma+} + I_{\sigma-})$, where $I_{\sigma+}$ and $I_{\sigma-}$ denote the intensity of the right ($\sigma+$) and left ($\sigma-$) circularly polarized emission. Similarly the linear PL polarization writes $P_l = (I_X - I_Y)/(I_X + I_Y)$ with $I_X$ and $I_Y$ the X and Y linearly polarized emission components.

Time-integrated PL spectra at T=4 K for a laser excitation energy $E_{\text{laser}}=1.851$ eV are presented in Fig. 1. Based on previous work [21,44,46], the two transitions are attributed to the direct ($E=1.711$ eV) and indirect (1.535 eV) exciton radiative recombination in WSe$_2$ bilayers, respectively. The PL excitation (PLE) spectrum in Fig. 1 for a detection energy set on the direct A-exciton transition ($E=1.711$ eV) exhibits a clear resonance for a laser energy $E_{\text{laser}}=2.13$ eV which corresponds to the excitation of the B-exciton. We find an SO-splitting energy between the A- and B-exciton of about 420 meV, in agreement with measurements in WSe$_2$ MLs [43].

Exciton dynamics and temperature dependence.— In Fig. 2a, the exciton kinetics for both optical transitions are displayed for T=4 K. Remarkably the indirect transition is characterized by a PL decay time ($\approx$ 25 ps) about one order of magnitude longer than the direct one. We find a very fast recombination time for the direct transition ($\lesssim$ 3 ps), as fast as the one measured for the neutral A-exciton in WSe$_2$ [30] and MoS$_2$ MLs [25,26]. This efficient and fast coupling to light of the direct transition explains the strong relative intensity of the direct transition in time-integrated PL compared to the indirect one observed in Fig. 1a. Ab-initio calculations performed on WSe$_2$ bilayers predict that the direct transition corresponds to recombination of both electrons and holes lying at the extrema of the conduction band (CB) and the valence band (VB) in the K valley [34,36,37]. The indirect transition is usually assigned to VB holes at the K point and CB electrons lying in a minimum energy point located between K and Γ points [38]. As an indirect transitions requires in addition absorption or emission of a phonon [39], the measurement of a 10-times longer PL decay time for the lowest energy transition in WSe$_2$ bilayers compared to the one measured in MLs supports our interpretation. As far as band structure calculations are concerned, note however that the strong Coulomb effects undoubtedly present in TMDC bilayers (with exciton binding energies 500 meV reported for MLs [14,18]) are not taken into account for the optical transitions.

The temperature dependence of the direct and indirect transition PL spectra is displayed in Fig. 2. Both transitions can be observed up to room temperature though there is a significant overlap in energy above 150 K. The clear observation of the direct transition for all temperatures demonstrates that the coupling to light (with a strong oscillator strength) of high energy carriers is comparable to the energy relaxation time down to k-valley point where the indirect transition occurs. We observe in Fig. 2a that this indirect transition is characterized by a decay time of about 25 ps, independent of the temperature in the range 4 to 150 K. For higher temperatures the lifetime determination is ambiguous due to the energy overlap of direct and indirect transitions.
exciton energy identified by Jones et al.\[21\]. We tentatively attribute the low PL polarization for excitonic transitions were only predicted for TMDC MLs\[3\], as inversion symmetry is globally restored for $2\text{H}$-bilayers. In that respect the large values of $P_c$ and $P_l$ in Fig. 3 are remarkable. The high $P_c$ and $P_l$ in time-integrated PL measurements of the direct transition of neutral or charged excitons in WSe$_2$\[21\] and WS$_2$\[22\] bilayers were interpreted recently as a consequence of the enhancement of the exciton spin lifetime. This is thought to be due to a spin-layer locking effect\[21\], where the exciton polarization is locked to the layer index i.e. its localization on the upper or lower layer. This is a fascinating subject for theory due the competition between the strong SO coupling (measured to be 420 meV in our sample in Fig. 1b), layer hopping energies and Coulomb effects\[21\] 23\] 24\] 41\]. Here time-resolved PL experiments are crucial and we demonstrate in Fig. 3: that $P_c$ of the direct transition decays within a few picoseconds, as fast as the PL intensity which is shown for comparison. This fast polarization decay could be due the large exciton exchange exchange interaction for excitons in bilayers (direct transition) similarly to the exciton depolarization evidenced recently in individual TMDC MLs\[43\] 45\]. In addition to polarization relaxation processes present already in isolated MLs, new depolarization channels open up in bilayers due to interlayer coupling\[21\] 23\]. Interestingly in Fig. 1, we observe a global minimum of $P_c$ of the A-exciton when the B-exciton is resonantly generated. One could speculate that at this energy interlayer hopping and spin flips, blocked by the SO interaction at lower energies, become more likely. Note that we do not observe in Fig. 3: the extremely long PL polarization decay time which should be the fingerprint of an excimer transition proposed by Yu et al.\[24\].

In conclusion, we have measured the exciton dynamics for both direct and indirect optical transitions in WSe$_2$ bilayers. These results reveal fast recombination times ($\lesssim 3$ ps and $\approx 25$ ps respectively) which should be taken into account to explain the unique spin polarization properties of the TMDC bilayers as well as the various proposed applications of such nanostructures including high temperature superfluidity based on indirect excitons\[40\].

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\[1\] A. K. Geim and I. V. Grigorieva, Nature 499, 419 (2013).
\[2\] X. Xu, D. Xiao, T. F. Heinz, and W. Yao, Nature Physics 10, 343 (2014).
\[3\] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, Phys. Rev. Lett. 105, 136805 (2010).
\[4\] A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, Nano Letters 10, 1271 (2010).
\[5\] D. Xiao, G.-B. Liu, W. Feng, X. Xu, and W. Yao, Phys. Rev. Lett. 108, 196802 (2012).
\[6\] T. Cao, G. Wang, W. Han, H. Ye, C. Zhu, J. Shi, Q. Niu, P. Tan, E. Wang, B. Liu, et al., Nature Communications
A. M. Jones, H. Yu, N. J. Ghimire, S. Wu, G. Aivazian, T. Cheiwchanchamnangij and W. R. L. Lambrecht, Phys. Rev. B 86, 081301 (2012).

G. Kioseoglou, A. T. Hanbicki, M. Currie, A. L. Friedman, D. Gunlycke, and B. T. Jonker, Applied Physics Letters 101, 221907 (pages 4) (2012).

A. M. Jones, H. Yu, N. J. Ghimire, S. Wu, G. Aivazian, J. S. Ross, B. Zhao, J. Yan, D. G. Mandrus, D. Xiao, et al., Nat. Nanotechnol. 8, 634 (2013).

K. F. Mak, K. L. McCull, J. Park, and P. L. McEuen, Science 344, 1489 (2014).

T. Cheiwchanchamnangij and W. R. L. Lambrecht, Phys. Rev. B 85, 205302 (2012).

H.-P. Komsa and A. V. Krasheninnikov, Phys. Rev. B 86, 241201 (2012).

K. He, N. Kumar, L. Zhao, Z. Wang, K. F. Mak, H. Zhao, and J. Shan, Phys. Rev. Lett. 113, 026803 (2014).

M. M. Ugeda, A. J. Bradley, S.-F. Shi, F. H. da Jornada, Y. Zhang, D. Y. Qi, S.-K. Mo, Z. Hussain, Z.-X. Shen, F. Wang, et al., Nature Materials doi: 10.1038/nmat4061 (2014).

A. Chernikov, T. C. Berkelbach, H. M. Hill, A. Rigosi, Y. Li, O. B. Aslan, D. R. Reichman, M. S. Hybertsen, and T. F. Heinz, Phys. Rev. Lett. 113, 076802 (2014).

Z. Ye, T. Cao, K. O’Brien, H. Zhu, X. Yin, Y. Wang, S. G. Louie, and X. Zhang, Nature 513, 214 (2014).

G. Wang, X. Marie, I. Gerber, T. Amand, D. Lagarde, L. Bouet, M. Vidal, A. Balocchi, and B. Urbaszek, e-print arXiv:1404.0056 (2014).

W. J. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D. A. Chenet, J. I. Dadap, I. P. Herman, et al., Phys. Rev. Lett. 111, 106801 (2013).

Y. Zhang, T.-R. Chang, B. Zhou, Y.-T. Cui, H. Yan, Z. Liu, F. Schmitt, J. Lee, R. Moore, Y. Chen, et al., Nature Nanotechnology 9, 111 (2014).

A. M. Jones, H. Yu, J. S. Ross, P. Klement, N. J. Ghimire, J. Yan, D. G. Mandrus, W. Yao, and X. Xu, Nat. Phys. 10, 130 (2014).

B. Zhu, H. Zeng, J. Dai, Z. Gong, and X. Cui, Proceedings of the National Academy of Sciences 111, 11606 (2014).

Q. Liu, X. Zhang, and A. Zunger, ArXiv e-prints (2014), 1408.6001.

T. Yu and M. W. Wu, Phys. Rev. B 90, 035437 (2014).

T. Korn, S. Heydrich, M. Hirmer, J. Schmutzler, and C. Schüller, Applied Physics Letters 99, 102109 (2011).

D. Lagarde, L. Bouet, X. Marie, C. R. Zhu, B. L. Liu, T. Amand, P. H. Tan, and B. Urbaszek, Phys. Rev. Lett. 112, 047401 (2014).

H. Shi, R. Yan, S. Bertolazzi, J. Brivio, B. Gao, A. Kis, D. Jena, H. G. Xing, and L. Huang, ACS Nano 7, 1072 (2013).

Q. Wang, S. Ge, X. Li, J. Qiu, Y. Ji, J. Feng, and D. Sun, ACS Nano 7, 11087 (2013).

C. Mai, A. Barrette, Y. Yu, Y. G. Semenov, K. W. Kim, L. Cao, and K. Gundogdu, Nano Letters 14, 202 (2014).

G. Wang, L. Bouet, D. Lagarde, M. Vidal, A. Balocchi, T. Amand, X. Marie, and B. Urbaszek, Phys. Rev. B 90, 075413 (2014).

P. Rivera, J. R. Schaibley, A. M. Jones, J. S. Ross, S. Wu, G. Aivazian, P. Klement, N. J. Ghimire, J. Yan, D. G. Mandrus, et al., ArXiv e-prints (2014), 1403.4985.

Y. Yu, S. Hu, L. Su, L. Huang, Y. Liu, Z. Jin, A. A. Purezky, D. B. Geohegan, K. W. Kim, Y. Zhang, et al., ArXiv e-prints (2014), 1403.6181.

B. Urbaszek, X. Marie, T. Amand, O. Krebs, P. Voisin, P. Maletinsky, A. Högele, and A. Imamoglu, Rev. Mod. Phys. 85, 79 (2013).

H. Sahin, S. Tongay, S. Horzum, W. Fan, J. Zhou, J. Li, J. Wu, and F. M. Peeters, Phys. Rev. B 87, 165409 (2013).

W. Zhao, Z. Ghorannevis, L. Chu, M. Toh, C. Kloc, P.-H. Tan, and G. Eda, ACS Nano 7, 791 (2013).

W. Zhao, R. M. Ribeiro, M. Toh, A. Carvalho, C. Kloc, A. H. Castro Neto, and G. Eda, Nano Letters 13, 5627 (2013).

L. Debibchi, O. Eriksson, and S. Lebègue, Phys. Rev. B 89, 205311 (2014).

The calculations of [24] suggest that the low energy PL transitions of [24] suggest that the low energy PL transitions are indirect in real space (type II), not k-space.

V. Harle, H. Bolay, E. Lux, F. Scholz, P. Michler, A. Moritz, T. Forner, and A. Hangleiter, in Indium Phosphide and Related Materials, 1994, Conference Proceedings., Sixth International Conference on (1994), pp. 6–9.

J. M. Riley, F. Mazzola, M. Dendzik, M. Michiardi, T. Takayama, L. Bawden, C. Granerod, M. Leanderson, T. Balasubramanian, M. Hoesch, et al., ArXiv e-prints (2014), 1408.6778.

X. Zhang, Q. Liu, J.-W. Luo, A. J. Freeman, and A. Zunger, Nat. Physics 10, 387 (2014).

We record a small but not zero linear polarization for a detection energy ≈ 1.63 eV, compare also with the shoulder in Fig. 3 on the P. Although not resolved in our PL spectrum, this energy was identified by Jones et al as impurity-bound excitons in WS2 bilayers [27].

M. M. Glazov, T. Amand, X. Marie, D. Lagarde, L. Bouet, and B. Urbaszek, Phys. Rev. B 89, 201302 (2014).

T. Yu and M. W. Wu, Phys. Rev. B 89, 205303 (2014).

C. R. Zhu, K. Zhang, M. Glazov, B. Urbaszek, T. Amand, Z. W. Ji, B. L. Liu, and X. Marie, ArXiv e-prints (2014), 1407.5862.

M. M. Fogler, L. V. Butov, and K. S. Novoselov, Nat Commun 5, 10.1038/ncomms5555 (2014).