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Magnetoluminescence and valley polarized state of a two-dimensional electron gas in WS_2 monolayers

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Materials often exhibit fundamentally new phenomena in reduced dimensions that potentially lead to novel applications. This is true for single-layer, two-dimensional semiconductor crystals of transition-metal dichalcogenides, MX_2 (M = Mo, W and X = S, Se). They exhibit direct bandgaps with energies in the visible region at the two non-equivalent valleys in the Brillouin zone. This makes them suitable for optoelectronic applications that range from light-emitting diodes to light harvesting and light sensors[1–7], and to valleytronics[8–17]. Here, we report the results of a magnetoluminescence study of WS_2 single-layer crystals in which the strong spin–orbit interaction additionally locks the valley and spin degrees of freedom. The recombination of the negatively charged exciton in the presence of a two-dimensional electron gas (2DEG) is found to be circularly polarized at zero magnetic field despite being excited with unpolarized light, which indicates that the existence of a valley polarized 2DEG is caused by valley and spin locking and strong electron–electron interactions.

Tungsten-based dichalcogenides, such as WS_2, belong to the same family as MoS_2 and have many similar properties[15–17]; both compounds have the same structure and, in single layers, exhibit luminescence around 2 eV at the K points. The primary difference between MoS_2 and WS_2 is the strength of the spin–orbit splitting because of the different sizes of the transition-metal atoms. The photoluminescence (PL) efficiency of WS_2 is found to be much higher than that of MoS_2. In addition, the emission linewidth of the former is narrower, which makes WS_2 a better candidate for optoelectronic applications.

Despite extensive studies of these systems, there is very limited work on the effects of the application of an external magnetic field[12,13]. The purpose of the work in Sallen *et al.*[12] and Zeng *et al.*[13] was to investigate the Hanle effect by applying an in-plane magnetic field and demonstrate the intriguing result of the absence of such an effect. Very recently, Zhang *et al.*[7] reported circularly polarized electroluminescence from WSe_2 p–i–n junctions; the authors explain their results in terms of the breaking of the valley symmetry by an in-plane electric field[7]. In this work, we report spontaneous circularly polarized light emission from a single WS_2 layer excited by linearly polarized light at zero magnetic field. We attribute this effect to the existence of a spontaneously valley polarized 2DEG; this new state becomes possible in 2D materials because of valley and spin coupling along with strong electron–electron interactions.

The PL emission was found to contain two features: (1) the neutral exciton X^0 and (2) a broad feature at a lower energy related to the recombination of a valence hole in the presence of pockets of 2DEG owing to unintentional doping, which we will broadly classify as the negatively charged exciton, X^-, or Fermi edge singularity in the presence of a strong disorder[18–20]. The X^- feature discussed here is much broader than the corresponding feature in $MoSe_2$ reported by Ross *et al.*[11] because of the finite 2DEG density. Both X^- and X^0 features, show clear signatures in the reflectance spectrum. At zero magnetic field the X^- feature, related to the 2DEG, is circularly polarized light with a polarization of up to 18%, in direct contrast to the X^0 emission, which has no polarization. The spontaneous polarization of the emitted PL, excited with linearly polarized light, is attributed to the existence of a valley polarized 2DEG.

In Fig. 1a, we show the zero magnetic field PL spectrum (black line) and the first derivative (blue line) of the reflectance spectrum at $T = 5$ K. A picture of the sample used in our experiment is shown in Fig. 1b with a magnification of 100. Raman spectroscopy was used to determine which portions of the flake were single layers[15,21]. The PL spectrum was excited using linearly polarized light at 488 nm with an excitation power density of 2.04×10^2 W cm^{-2}. The strong PL emission below the free exciton energy is associated with the recombination of valence holes with a 2DEG present in different regions of the sample. In other words, the trion state has to be considered in the presence of a significant number of extra electrons distributed over different valley and spin states. In a material like GaAs, such a dense electron gas would lead to the breakdown of the trion and result in a Fermi-edge singularity. In transition-metal dichalcogenides, the binding energy of the exciton and the trion are much larger than those in materials such as GaAs; thus we expect the trion to be stabilized for much larger electron densities. The emission spectrum contains two features, labelled as X^0 and X^-. The identification of X^0 (at 2.053 eV) and X^- (at 2.014 eV) was made on the basis of previous work[22] as well as the fact that both X^0 and X^- have strong signatures in the reflectance spectrum[23].

One possible model that explains the coexistence of X^0 with the 2DEG feature is that the WS_2 crystal is inhomogeneous, possibly because of the inhomogeneous strain imposed by the substrate. This results in distinct regions: (1) regions with a different electron density from which we obtain the X^-–2DEG emission, and (2) regions with no electrons from which we obtain the X^0 emission, as extensively studied by a number of groups investigating gate-controlled 2DEG in semiconductor quantum wells[18–20]. The evolution of the PL with increasing temperature is shown in Fig. 1c for the $5\ \mathrm{K} < T < 90\ \mathrm{K}$ temperature range. It is clear from this

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