Monolayer MoSe$_2$ and other monolayer transition metal dichalcogenides (TMDs) are a materials system with unique potential for controlling their valley degree of freedom [1–8]. Similar to graphene, the conduction and valence band show extrema (valleys) at the vertices of a hexagonal Brillouin zone; unlike graphene, MoSe$_2$ exhibits a nonzero optical gap of 1.66 eV [9,10]. This has allowed exploration of optoelectronic properties arising from the valley-dependent chirality of massive Dirac fermions predicted in the context of inversion symmetry broken graphene [11,12]. This chirality leads to optical selection rules coupling the exciton valley degree of freedom to photon handedness [2–7]. Using polarization-resolved spectroscopy, researchers have demonstrated valley-selective luminescence with near 100% fidelity [2,7]. Furthermore, the ability to pump valley-polarized carriers with circularly polarized light has been demonstrated through the valley Hall effect [8]. The chiral electronic states are also predicted to possess valley-contrasting orbital magnetic moments coupling valley pseudospin to magnetic field [11–17], which opens up the possibility for magnetic control over the valley degree of freedom [13,18].

Here, we demonstrate the use of magnetic fields to break valley degeneracy in a monolayer TMD. Specifically, we report polarization-resolved luminescence spectra for back-gated MoSe$_2$ devices at 4.2 K and in magnetic fields up to 6.7 T. We study the luminescence peak energies as a function of magnetic field, finding a linear splitting of $-0.22$ meV/T between peaks corresponding to light emission with different senses of circular polarization, $\sigma_+$ and $\sigma_-$. We interpret this as a Zeeman splitting due to valley-dependent magnetic moments. We also investigate the magnetic-field dependence of luminescence handedness, finding that the emission becomes circularly polarized in a magnetic field even with unpolarized excitation and that the degree of this polarization can be increased to about 50% by gating the sample. This suggests that electric fields can facilitate the generation of valley-population imbalance in samples where valley degeneracy has been broken by a magnetic field. Our results demonstrate a recently proposed [18] strategy for generating valley populations and could lead to new approaches for controlling the valley degree of freedom in monolayer TMDs.

Using polarization-resolved photoluminescence spectroscopy, we investigate the breaking of valley degeneracy by an out-of-plane magnetic field in back-gated monolayer MoSe$_2$ devices. We observe a linear splitting of $-0.22$ meV/T between luminescence peak energies in $\sigma_+$ and $\sigma_-$ emission for both neutral and charged excitons. The optical selection rules of monolayer MoSe$_2$ couple the photon handedness to the exciton valley degree of freedom; so this splitting demonstrates valley degeneracy breaking. In addition, we find that the luminescence handedness can be controlled with a magnetic field to a degree that depends on the back-gate voltage. An applied magnetic field, therefore, provides effective strategies for control over the valley degree of freedom.
coupling linearly polarized light into one of the two fiber polarization modes, or create equal intensity excitation in $\sigma_+$ and $\sigma_-$ polarization by coupling in light polarized at 45° to the fiber axes. We excite luminescence with light from a 1.89 eV laser diode, which is 230 meV blueshifted from the A exciton transition, and as a result, we see little dependence of the emission polarization on excitation polarization (see the Supplemental Material, Sec. 1 [21]). The conclusions discussed below are independent of excitation polarization.

To fabricate our samples, we exfoliate bulk MoSe$_2$ crystals (grown by direct vapor transport) onto 300 nm silicon oxide on silicon then use electron-beam lithography to define a single 0.5 nm Ti and 75 nm Au contact, allowing the use of the silicon substrate as a back gate. All data shown in the main text were taken from devices D1 and D2 pictured in Fig. 1(c). Figure 1(d) shows the $B = 0$ luminescence spectra of D2 at $-30$, 0, 10, and 50 V. The peaks at 1.66 and 1.63 eV correspond to the neutral and charged A exciton, respectively, with a charged exciton (trion) binding energy of 30 meV [9]. As the back-gate voltage is increased, the exciton luminescence decreases and the trion luminescence increases, showing that our samples are intrinsically $n$ type and that the 1.63 eV peak corresponds to negatively charged trion luminescence.

Figure 2(a) compares polarization-resolved spectra taken for D1 in out-of-plane magnetic fields of 0, 6.7, and $-6.7$ T and with the back gate grounded. For these data, we excite photoluminescence using equal intensity excitation in $\sigma_+$ and $\sigma_-$ polarization. At zero field, we find no significant dependence of the peak energies or intensities on emission handedness. In comparison, the spectra taken at 6.7 T show splitting between the $\sigma_+$ and $\sigma_-$ emission peaks of about $-1.5$ meV for both the exciton and trion. The luminescence is also $\sigma_+$ polarized: the trion peak has $P_{\text{trion}} = (I_+ - I_-)/(I_+ + I_-) = 14\%$, where $I_\pm$ is the peak intensity of the trion found with $\sigma_\pm$ detection. For the exciton, we measure $P_{\text{exciton}} = 9\%$. The luminescence polarization changes sign with reversal of the magnetic field but not with excitation polarization, showing that it arises from magnetically induced changes in the exciton and trion populations. Figure 2(b) depicts the schematic band structure of a MoSe$_2$ monolayer, illustrating the direct band gaps at the $K_+$ and $K_-$ points, with arrows indicating the allowed $A$ exciton transitions for $\sigma_\pm$ light. Since the emission handedness is coupled to the exciton valley degree of freedom, the peak splitting and polarization we observe indicate valley degeneracy breaking.

FIG. 1 (color online). (a) Experimental geometry showing back-gated monolayer MoSe$_2$ devices in out-of-plane magnetic fields. Luminescence is excited with light from a 1.89 eV laser diode and collected separately for $\sigma_+$ and $\sigma_-$ polarization in the Faraday geometry. (b) Schematic of the fiber-coupled optical cryostat used in the experiment. (c) Optical micrographs of devices D1 and D2. (d) Luminescence spectra of D2 taken at 0 T and 4.2 K with $-30$, 0, 10, and 50 V back-gate voltage.
Figure 3(a) shows the valley splitting of the exciton and trion peaks, defined as the difference between peak energies found with $\sigma_+$ and $\sigma_-$ detection, versus the magnetic field. For each data point, the peak positions were extracted via fits to a phenomenological asymmetric Voigt line shape (see the Supplemental Material, Sec. 2 [21]). The error bars come primarily from the CCD pixel size (about 0.15 nm per pixel). For both the exciton and trion peaks, the valley splitting shows a linear magnetic-field dependence with a slope of $-0.22 \pm 0.01$ meV/T. Similar results were found on three separate samples; data from other samples are given in the Supplemental Material, Sec. 3 [21].

Valley splitting in a magnetic field arises from the intrinsic chirality of Bloch electrons at the points. States at the two valley edges are Kramers doublets related by time-reversal symmetry, so that their degeneracy can be broken by breaking time-reversal symmetry. Bloch electrons in a given band carry spin and orbital magnetic moments which change sign between valleys [11–13,42]. Figure 3(b) schematically shows the energy shifts arising from Zeeman coupling between these moments and the magnetic field; there, we define $2E_Z^{(v)}$ as the magnetic-field-induced energy difference between the $K_+$ and $K_-$ valley at the conduction (valence) band edge. Magnetoluminescence spectroscopy probes only the exciton Zeeman energy, which is the difference between the conduction and valence band Zeeman energies. In this difference, the contributions from spin magnetic moments are expected to cancel, leaving only the contributions from orbital magnetic moments.

The measured sign and magnitude of the valley splitting can be understood within a tight-binding picture [43,44]. In the $K_c$ valley (letting $\tau = \pm 1$ be the valley quantum number), the valence band arises from hybridization of $d_{\sigma \gamma} + t_i d_{\alpha \nu}$ orbitals with angular momentum $l_i = 2r h$, while the conduction band arises from hybridization of $d_z$ orbitals with $l_z = 0$ [1,6,41,45]. In the tight-binding limit, we, therefore, expect a contribution to the exciton Zeeman energy of $2(E_{v,a} - E_{v,a}^{(v)}) = -4\mu_mB$ from atomic-scale magnetic moments. The phase winding of Bloch states on the intercellular scale can also add to the orbital magnetic moment [11,42–44,46]. For example, in the two-band tight-binding model (the massive Dirac fermion model), the intercellular magnetic moment is the same for the conduction and valence bands with value $-\tau \mu_B(m_e/m_g)$, where $m_e$ is the free-electron mass, and $m_g$ is the electron-hole symmetric carrier effective mass [11,12]. Including the spin magnetic moments, this gives a total Zeeman splitting of $2E_Z = 2\mu_B + 2\mu_B(m_e/m_g)$ for the conduction band and $2E_Z^v = 2\mu_B + 4\mu_B B + 2\mu_B B(m_e/m_g)$ for the valence band, and as a result, $2E_Z = 2E_Z^v = -4\mu_mB$ (i.e., there is no net intercellular contribution). In more general hopping models, the conduction and valence bands can have different intercellular moments giving a net contribution to the exciton magnetic moment [16,40,43,44].

To compare our measurements with theory, we define the exciton valley $g$ factor $g_{vex}^{val}$ as

$$g_{vex}^{val} = \frac{2(E_+ - E_-)}{\mu_B B} = \frac{2(E_Z^v - E_Z)}{\mu_B B},$$

where $E_{\pm}$ is the measured exciton peak energy in the $\sigma_{\pm}$ detection. Our exciton valley splitting measurements correspond to $g_{vex}^{val} = -3.8 \pm 0.2$, consistent with the value of $g_{vex}^{val} = -4$ expected from the $d$-orbital contribution to the exciton magnetic moment. Any deviation of $g_{vex}^{val}$ from $-4$ theoretically corresponds to the intercellular contribution to the $g$ factor. Our results, therefore, suggest that the intercellular contribution to $g_{vex}^{val}$ is small in the case of MoSe$_2$. We also expect the trion to have approximately the same splitting as the exciton, evinced by considering the trion as an exciton bound to an additional electron. While the additional electron contributes to the trion magnetic moment, it contributes equally to the final state moment after recombination, leaving the transition energy unaffected (as discussed in more detail in the Supplemental Material, Sec. 4 [21]). This is consistent with the experimental results of Fig. 3(a) for zero applied gate voltage.

We also attempted to calculate the valley $g$ factor using the multiband $\mathbf{k} \cdot \mathbf{p}$ theory of Ref. [13], since this theory should include the intercellular and atomic contributions in a unified way [46]. The need to discuss these terms separately...
is an artifact of the lattice models discussed above. The calculation is detailed in Sec. 5 of the Supplemental Material [21] and gives a value for $g_{\text{trion}}$ similar in magnitude to our experimental results, but with the opposite sign (see the Supplemental Material, Sec. 6 for our experimental determination of the sign [21]). Therefore, further theoretical work is required to understand the exciton valley splitting within the context of $k \cdot p$ theory calculations.

We find that the trion valley splitting and the resulting luminescence polarization both show a surprising dependence on an applied back-gate voltage. Polarization-resolved spectra taken with −20 and 51 V applied to the substrate are shown in Fig. 4(a) for device D2. Our samples show significant hysteresis assumed to arise from photoionization of trap states [47], and the data in this panel are taken from a downward sweep. Figure 4(b) shows the trion splitting versus magnetic field for two different gate voltages on a downward sweep, finding $-0.29 \pm 0.02$ meV/T at 40 V and $-0.23 \pm 0.02$ meV/T at 0 V. This gate-voltage dependence of the trion splitting could arise from carrier-density dependence of the band Zeeman energies [11,16], a hot luminescence effect as discussed in Sec. 4 of the Supplemental Material [21] or other effects resulting from changes in the trion or final state wave functions upon increasing the Fermi level [48].

The degree of trion polarization as a function of gate voltage is shown in Fig. 4(c). In this data set, we find a trion polarization that increases from 18% near zero back-gate voltage to over 50% near 40 V. The luminescence polarization in the n-type regime is related to the populations of different trion species via $P_{\text{trion}} = (n_+ - n_-) / (n_+ + n_-)$, where $n_\pm$ is the density of negatively charged trions with their hole in valley $K_\pm$ (i.e., those which emit $\sigma_\pm$-polarized light upon recombination, which we refer to as $K_\pm$ valley trions). The sign of $P_{\text{trion}}$ is found to be independent of the excitation polarization and instead follows the sign of the magnetic field, and we, therefore, interpret the magnetic-field dependence of the trion polarization as arising from partial relaxation of trions into their lowest energy spin-valley configuration (qualitatively consistent with the dependence of trion polarization on excitation power, see the Supplemental Material, Sec. 7 [21]). This relaxation is expected to be incomplete, as the intervalley scattering time is longer than the recombination time [2]. In Sec. 4 of the Supplemental Material, we calculate the trion polarization within a simple rate-equation model and show that the observed $P_{\text{trion}}$ implies a ratio of the recombination time to the intervalley scattering time of $\sim 0.2$ at low carrier density [21]. This is about an order of magnitude larger than the value found in time-resolved measurements for WSe$_2$ at zero magnetic field [49]; however, the time-resolved measurements used resonant excitation which is expected to lead to reduced intervalley scattering compared to the off-resonant excitation we use. Trions can scatter between valleys via spin-flip intervalley scattering of their hole, and if this is the dominant scattering mechanism, our results imply that the hole intervalley scattering rate increases monotonically with carrier density. This is consistent with the Bir-Aronov-Pikus mechanism for intervalley scattering of holes via their exchange interaction with the conduction electrons [2,50]. The data in Fig. 4(c) were taken with $\sigma-$ excitation, but similar results were found using unpolarized excitation (see Sec. 3 of the Supplemental Material [21]).

In summary, we have presented measurements of polarization-resolved luminescence spectra for MoSe$_2$ at 4.2 K in magnetic fields up to 6.7 T, demonstrating valley degeneracy breaking. We have measured a splitting of $-0.22 \pm 0.01$ meV/T between exciton peaks in $\sigma_+$- and $\sigma_-$-polarized emission spectra. This value is consistent with a simple tight-binding picture of the MoSe$_2$ band structure. We have also observed gate dependence of the trion valley splitting and polarization. Even with off-resonant unpolarized excitation, we were able to achieve a trion circular polarization of about 50% by gating the sample in a 6.7 T magnetic field. The application of magnetic and electric fields can, therefore, provide an effective strategy for manipulating the valley degree of freedom in monolayer TMDs.

Similar work on WSe$_2$ has recently been posted by the Washington group [44] and the ETH Zurich group [43].

We thank Kathryn McGill and Joshua Kevek for growth of the bulk MoSe$_2$ crystal used for this work. We also thank Guido Burkard, Péter Rakyta, Alexander Högele, and...
Ermin Malic for helpful discussions. This research was supported in part by the NSF (Grant No. DMR-1010768) and the Kavli Institute at Cornell for Nanoscale Science. We also made use of the Cornell Center for Materials Research Shared Facilities which are supported through the NSF Materials Research and Engineering Center program (Grant No. DMR-1120296). Device fabrication was performed at the Cornell NanoScale Facility, a member of the National Nanotechnology Infrastructure Network, which is supported by the National Science Foundation (Grant No. ECCS-0335765). D. M. acknowledges support of Canada Postgraduate Scholarship.