Electron-electron (e-e) interactions underpin many interesting phenomena in 2D layers of mobile charges, including the fractional quantum Hall effect \(1\), spin textures (skyrmions) \(2\), and quantum Hall ferromagnetism \(3\). These phenomena arise from the Coulomb repulsion between charges, which in turn typically enhances the susceptibility of spin or related pseudospin (e.g., valley, layer, subband) degrees of freedom \(\Xi\), and can even cause instabilities and spontaneous transitions to broken-symmetry phases \(7,10\). Such interactions have been studied in 2D electron and hole gases (2DEGs, 2DHGs) in conventional Si, GaAs, and AlAs semiconductors \(11–17\) (and also in graphene \(13,19\)), usually deep in the quantum regime at high magnetic fields \(B\) where only a few Landau levels (LLs) are occupied. Studies in tilted \(B\) have proven indispensable in these materials \(11–14,17\), because they provide a means to tune orbital (cyclotron) and spin (Zeeman) energies independently, thereby allowing to align LLs with different quantum numbers, so that e-e interactions can manifest most clearly.

In the newer family of monolayer transition-metal dichalcogenide (TMD) semiconductors such as MoS\(_2\) and WSe\(_2\) \(20–24\), advances in material quality have enabled high-mobility 2DEGs and 2DHGs \(25\). Owing to large carrier masses and reduced dielectric screening, e-e interactions are anticipated to be strong, even at high carrier densities. Of particular interest, band extrema lie at the inequivalent \(K\) and \(K'\) points (valleys) of the Brillouin zone, providing exciting opportunities to study both spin and valley degrees of freedom in doped monolayer systems. Indeed, recent transport \(20,29\), optical \(30–35\), and compressibility \(36\) studies revealed the expected \(37,38\) spin- and valley-polarized LLs and related quantum oscillations in large \(B\), and enhanced valley susceptibilities have been inferred. However, because spins in TMD monolayers are locked out-of-plane by strong spin-orbit coupling, tilted-\(B\) methods cannot align LLs with different valley/spin index \(26,29\). To date this has limited studies of predicted \(39,42\) valley/spin instabilities and phase transitions arising from e-e interactions.

Using a hole-doped WSe\(_2\) monolayer, here we demonstrate and then exploit the density-tunable enhancement of the valley Zeeman energy to align LLs in the \(K\) and \(K'\) valleys. Under these conditions, the 2DHG becomes unstable and exhibits spontaneous valley polarization. To observe this we measure absorption spectra in large magnetic fields to 60 T, and find well-resolved sequences of optical transitions in both \(\sigma^+\) and \(\sigma^-\) circular polarizations. Due to the valley-specific optical selection rules, this allows to unambiguously and separately determine the number of filled LLs in \(K\) and \(K'\), and find that the 2D hole gas becomes unstable against small changes in LL filling and can spontaneously valley-polarize. These results cannot be understood within a single-particle picture, highlighting the importance of exchange interactions in determining the ground state of 2D carriers in monolayer semiconductors.
ulate the valence bands and the positively-charged trion appears at lower energy ($\approx 1.70$ eV). Similar maps have been reported recently [30, 34, 33]; the narrow features observed here confirm the high quality of our sample-on-fiber assembly. These features can also be described as many-body exciton-polarons [31, 33, 44–47]. That is, an electron-hole pair photoexcited into an existing Fermi sea will be dressed by interactions with the mobile carriers in the opposite valley, leading to distinct “attractive” and “repulsive” branches of the exciton-polaron quasiparticle. At low carrier densities, these branches equate with the lower-energy trion and higher-energy exciton, respectively. As density increases, the repulsive branch blueshifts and fades as all the oscillator strength shifts to the lower-energy attractive branch.

We focus henceforth on $p$-type WSe$_2$ because it provides an especially simple realization of a two-valley system: The huge 450 meV spin-orbit splitting between the spin-up and -down valence bands in $K$ and $K'$ ensures that only the topmost band in each valley plays a role, even at the largest $p$ and $B$.

Essential to our main goal of controlling the LL alignment in the two valleys is the ability to measure – unambiguously and separately – the number of filled LLs. As direct reporters of these values we use the bare exciton transition (in $K$), and the attractive polaron transition (in $K'$), as described below. This approach exploits the optical selection rules in monolayer TMDs, whereby transitions in $K$ and $K'$ couple selectively to $\sigma^+$ and $\sigma^-$ circularly polarized light. We emphasize that optical studies are therefore distinct from electrical measurements of quantum oscillations [20, 29, 36], which reveal overall LL filling factors but do not a priori indicate in which valley the various LLs reside. Importantly, we also rely on large $B$ to work in the well-resolved quantum regime, where only a few LLs are occupied (even at large $p$) and interactions are strongest [3], and where spectral signatures from different LLs are distinct.

Figure 2 shows maps of the absorption spectra versus $B$, at selected $p$. Optical transitions in the $K(K')$ valley are revealed in $\sigma^-(\sigma^+)$ polarization, obtained in $+B(-B)$ [38].

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FIG. 1. (a) The dual-gated WSe$_2$ monolayer-on-fiber assembly used for absorption spectroscopy in pulsed magnetic fields $B$ to $\pm 60$ T. (b) A $B=0$ map of the absorption spectra ($1-\frac{1}{e^2}$) vs. gate voltage $V_g$ at 4 K. $T$ and $T_0$ are transmission and reference spectra.
I, $\sigma^+$, and through the attractive polaron resonances in Fig. 2(f) (regime II, $\sigma^-$), respectively. Both show $1/B$-periodic Shubnikov-de Haas (SdH) type oscillations. Minima occur when the indicated LL is filled, and correspond to the arrows shown on the absorption maps. In regime I, adjacent minima change the overall filling factor $\nu$ by one (because only $K$ is occupied), whereas adjacent minima in regime II change $\nu$ by two (because both valleys are occupied).

Importantly, Fig. 3(c) shows that for a given $p$, minima in both $\sigma^\pm$ (red and blue points) can be combined and fit to the single line given by $\nu = \hbar p/eB$, where $\nu = 2.415 \times 10^{10} \text{ cm}^{-2}\text{T}^{-1}$ is the LL degeneracy. This confirms the enumeration of filled LLs and determines $p$. Moreover, these data also reveal $N_p$, the number of LLs in $K$ that must be filled before any LL in $K'$ is filled. As discussed above, we determine $N_p=8$ when $p$ is small ($< 3 \times 10^{12} \text{ cm}^{-2}$), indicating a large $E_Z$ and enhanced $g_\sigma^p$. However, as shown in Fig. 3(d), $N_p$ falls from 8 to 5 as $p$ increases to $\approx 7 \times 10^{12} \text{ cm}^{-2}$, revealing that $E_Z$ and therefore $g_\sigma^p$ are strongly dependent on $p$. The density-dependent valley susceptibility and ordering of the LLs, depicted in Fig. 3(d), is unambiguously observed here via optical spectroscopy for the first time. These results are consistent with recent reports of odd-even orderings of SdH oscillations [26, 29, 36], and in line with the expectation that $e-e$ interactions increase at small $p$ [6, 14]. Figure 3(d) also shows the dimensionless interaction parameter $r_s = m_0 e^2/(\hbar^2 k_\sigma \sqrt{\pi p})$, which characterizes the ratio of Coulomb to kinetic (Fermi) energy [5], where $\kappa=3$ is the hBN dielectric constant. $r_s \approx 1$ even at large $p$, which anticipates the important role of $e-e$ interactions.

Having established the interdependence between $g_\sigma^p$, $\nu$, $B$, and $p$, we now focus on the central goal: aligning LLs in $K$ and $K'$ so that $e-e$ interactions can potentially drive instabilities in the valley pseudospin. Historically, this was often achieved by tilting $B$ to tune LLs with different spin into alignment [3, 11–14, 17]. In TMD monolayers where spins are locked out-of-plane, alternative approaches are required. We therefore exploit the dependence of $E_Z$ and $g_\sigma^p$ on $p$. Figure 3(d) shows that LLs in $K$ and $K'$ will align only at certain $p$ where $E_Z$ is a multiple of the cyclotron energy (equivalently, when $N_p$ changes). Using $m_0 = 0.5m_0$, this conveniently occurs when $g_\sigma^p$ is an even integer.

Instabilities will be most apparent at large $B$, where transitions from adjacent LLs are well-resolved spectrally. We therefore tune $p \approx 5 \times 10^{12} \text{ cm}^{-2}$, so that $g_\sigma \approx 10$ and $B_c \approx 40$ T. And indeed, under these conditions, we find that signatures of instability and spontaneous valley polarization are observed in the expanded $\sigma^-$ map of Fig. 4(a). In marked contrast to maps at larger and smaller $p$ that show a smooth and systematic progression of resonances as the 2DHG enters the mixed regime.
[e.g., Figs. 2 (b,e)], Fig. 4(a) shows that as $|B|$ decreases from 40→30 T, the $\sigma^-$ absorption jumps back and forth between discrete values, revealing the filling, sudden depopulation, and re-filling of the uppermost $-1K'$ LL, indicating spontaneous valley polarization.

This unusual pattern can be understood as follows: Initially, LLs in $K$ and $K'$ are ordered as drawn in Fig. 4(c): $g_{1}''$ is slightly less than 10, so that $-1K'$ resides slightly above $-6K$. At large $|B|$, the 2DHG is fully polarized and the only $\sigma^-$ absorption is the attractive polaron originating from the (unoccupied) $-1K'$. As $|B|$ falls below $\sim$40 T, the 2DHG enters the mixed regime II as $-1K'$ begins to fill with holes (point “a” on the map). When it fills completely (point “b”), absorption from $-1K'$ ceases and absorption from $-2K'$ commences, as described above and as drawn in Fig. 4(d). Crucially, however, at $\sim$34 T (point “c”), absorption from $-2K'$ abruptly and unexpectedly ceases, and absorption from $-1K'$ reappears. This indicates that $-1K'$ has at least partially emptied, and that the holes have transferred to $-6K$, discontinuously lowering the net $e-e$ interaction energy by maximizing the total spin/valley polarization. This can be regarded [5] as an abrupt jump in $g_{1}''$ to a value slightly larger than 10, which re-orders the LLs [see Fig. 4(e)]. As $|B|$ decreases further, $-1K'$ eventually must fill again and its associated absorption ceases once again, while absorption from $-2K'$ re-commences (point “d”). Thus, the two fields at which absorption from $-1K'$ cease ($\sim$35 T and $\sim$30 T) correspond to $\nu=7$ and $\nu=8$. Moreover, although not as clearly resolved, a similar sequence of disappearing and reappearing absorption transitions is observed at lower fields whenever the $-i^{th}$ LL in $K'$ (which is nearly degenerate with the $-(i+5)^{th}$ LL in $K$) fills with holes. By counting all these transitions, all $\nu$ up to 17 can be fit as shown in Fig. 4(b). This instability, observed in p-type WSe$_2$ via its selective influence on the attractive exciton-polaron optical transitions, provides direct evidence for a spontaneous and discontinuous change in valley polarization in a monolayer TMD semiconductor, analogous to the transition to the quantum Hall ferromagnet state studied in conventional semiconductors [3, 11, 16, 17].

Based on Fig. 3(d), instabilities can also be expected when $N_p$ drops from 8→7 ($p \approx 3 \times 10^{12}$). However, at this point $B_c \sim 18$ T, which is not sufficient to spectrally resolve adjacent LLs in this sample – although the data do suggest an anomaly (Supplemental Fig. S2). Similarly, instabilities may occur at larger $p \approx 7 \times 10^{12}$ (when $N_p$ drops from 6→5), but we did not observe it, possibly because $r_s$ is too small at this larger $p$ for $e-e$ interactions to dominate.

These results indicate that the valence bands of monolayer TMDs represent a rich platform from which to study emergent phases arising from $e-e$ interactions. We emphasize that the ability to unambiguously detect abrupt changes in the 2DHG valley polarization derives from the utility of polarized optical methods, which complement electrical measurements through their ability to separately distinguish carriers in each valley. Recent electrical measurements of SdH oscillations in various doped TMD monolayers have shown non-vanishing SdH minima.
when LLs are believed to align [28, 29, 30], which is (at least) consistent with hybridization and anticrossing of degenerate LLs in $K$ and $K'$, and may also be consistent with a discontinuous jump in the LL ordering [11]. Our polarized optical studies support the latter scenario. However, whether the valley instability that we clearly observe at $\approx 35 \, T$ represents an true first-order phase transition remains an open question; careful transport studies in this field and doping regime—and in particular the presence or absence of hysteretic resistance [10, 17]—could answer this question.

We thank Wang Yao, Jun Zhu, Bernhard Urbaszek, and Xavier Marie for helpful discussions. Work at the NHMFL was supported by the Los Alamos LDRD program and the DOE BES Science of 100 T program. The NHMFL is supported by National Science Foundation (NSF) DMR-1644779, the State of Florida, and the U.S. Department of Energy (DOE). Work at the University of Washington was supported by the DOE Basic Energy Sciences, Materials Sciences and Engineering Division (Grant No. de-sc0018171).
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Supplemental Fig. S1. Maps of the $\sigma^\pm$ absorption spectra $(1-T/T_0)$ vs. $B$ up to ±60 T for all measured hole densities $p$. Densities $p \leq 1.4 \times 10^{12}$ cm$^{-2}$ are estimated by linear extrapolation of $p$ vs. $V_g$ relation. $\sigma^+$ ($\sigma^-$) polarized spectra, i.e., from the $K$ ($K'$) valley, are observed at $+B$ ($-B$). Horizontal lines separate the “fully-polarized” regime I (|$B$| > $B_c$) from the “mixed” regime II (|$B$| < $B_c$). As in Fig. 2 of the main text, arrows show where the indicated LL in the $K$ valley is completely filled with holes. At low $p$, we can track the filling down to the lowest 0$K$ level.

**FIG. 5.** Supplemental Fig. S1: Maps of the $\sigma^\pm$ absorption spectra $(1-T/T_0)$ vs. $B$ up to ±60 T for all measured hole densities $p$. Densities $p \leq 1.4 \times 10^{12}$ cm$^{-2}$ are estimated by linear extrapolation of $p$ vs. $V_g$ relation. $\sigma^+$ ($\sigma^-$) polarized spectra, i.e., from the $K$ ($K'$) valley, are observed at $+B$ ($-B$). Horizontal lines separate the “fully-polarized” regime I (|$B$| > $B_c$) from the “mixed” regime II (|$B$| < $B_c$). As in Fig. 2 of the main text, arrows show where the indicated LL in the $K$ valley is completely filled with holes. At low $p$, we can track the filling down to the lowest 0$K$ level.
FIG. 6. **Supplemental Fig. S2:** Possible indications of the additional valley polarization instability that is expected at lower hole density ($p \sim 3 \times 10^{12} \text{ cm}^{-2}$), when $N_p$ drops from 8 to 7. Expanded $\sigma^-$ absorption maps at (a) $p = 3.30 \times 10^{12} \text{ cm}^{-2}$ and (b) $3.90 \times 10^{12} \text{ cm}^{-2}$. In marked contrast to the map on the right, which shows a smooth and systematic progression of the resonances as the 2DHG sequentially fills the LLs in the $K'$ valley, the absorption line in the map on the left appears to more abruptly jump back and forth between discrete values (analogous to the instability shown in Fig. 4 of the main text). This instability is expected to occur when the $-1K'$ level in the $K'$ valley aligns with the $-7K$ level in the $K$ valley (i.e., when $p \sim 3 \times 10^{12} \text{ cm}^{-2}$, and $N_p$ changes from 8 to 7). However, at this lower carrier density the $-1K'$ level fills at around $B_c = 18 \text{ T}$, and at this lower field the LLs are not sufficiently separated in energy to unambiguously resolve them in optical spectra. The oval shape drawings are guides to the eye of the resonance maps at (a) $p = 5.55 \times 10^{12} \text{ cm}^{-2}$ and (b) $3.90 \times 10^{12} \text{ cm}^{-2}$. In marked contrast to the map on the right, which shows a smooth and systematic progression of the resonances as the 2DHG sequentially fills the LLs in the $K'$ valley, the absorption line in the map on the left appears to more abruptly jump back and forth between discrete values (analogous to the instability shown in Fig. 4 of the main text). This instability is expected to occur when the $-1K'$ level in the $K'$ valley aligns with the $-7K$ level in the $K$ valley (i.e., when $p \sim 3 \times 10^{12} \text{ cm}^{-2}$, and $N_p$ changes from 8 to 7). However, at this lower carrier density the $-1K'$ level fills at around $B_c = 18 \text{ T}$, and at this lower field the LLs are not sufficiently separated in energy to unambiguously resolve them in optical spectra. The oval shape drawings are guides to the eye of the $\sigma^-$ absorption features. White, green and magenta color represents attractive polaron absorption from the $-1K'$, $-2K'$, and $-3K'$ LLs, respectively.

FIG. 7. **Supplemental Fig. S3:** Comparison of the raw (unsmoothed) $\sigma^-$ absorption maps at $p = 5.55 \times 10^{12} \text{ cm}^{-2}$, taken during a single magnetic field pulse when (a) $B$ sweeps quickly up to peak field ($-60 \text{ T}$) and (b) when $B$ sweeps more slowly back down to zero field. Data shown in the main text is always acquired during the downsweep, where $B$ changes much less during the 0.5 ms spectral acquisition time (which is the fastest acquisition time of our CCD camera). (c) Field profile of the capacitor driven pulsed magnet, which has a fast upsweep and slow downsweep. Points show the average field at which each spectra was taken. The field is changing too rapidly during the upsweep to spectrally resolve the jumps in the absorption lines that are clearly resolved during the downsweep, precluding any quantitative analysis of possible hysteretic effects associated with spontaneous valley polarization.