Spectroscopic evidence for a spin and valley polarized metallic state in a non-magic-angle twisted bilayer graphene

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In the magic-angle twisted bilayer graphene (MA-TBG), strong electron-electron (e-e) correlations caused by the band-flattening lead to many exotic quantum phases such as superconductivity, correlated insulator, ferromagnetism, and quantum anomalous Hall effects, when its low-energy van Hove singularities (VHSs) are partially filled. Here our high-resolution scanning tunneling microscope and spectroscopy measurements demonstrate that the e-e correlation in a non-magic-angle TBG with a twist angle $\theta = 1.49^\circ$ still plays an important role in determining its electronic properties. Our most interesting observation on that sample is that when one of its VHS is partially filled, the one associated peak in the spectrum splits into four peaks. Our analysis based on the continuum model suggests that such a one-to-four split of the VHS originates from the formation of an interaction-driven spin-valley-polarized metallic state near the VHS, lifting both the spin and valley degeneracies. Our results for this non-magic-angle TBG reveal a new symmetry-breaking phase, which has not been identified in the MA-TBG or in other systems.
Twisted bilayer graphene (TBG) is a particularly interesting van der Waals structure with two low-energy van Hove singularities (VHSs) that can be tuned by a relative twist angle $\theta$ between the two graphene layers\textsuperscript{1-6}. When the twist angle is tuned to near the so-called magic angle (MA) ($\theta \sim 1.1^\circ$), the two VHSs merge into 8 nearly flat bands around charge neutrality which are well separated from the high-energy bands\textsuperscript{7-10}. When these in-gap flat bands are partially filled, strong electron-electron (e-e) correlation drives many exotic quantum phases, including superconductivity, correlated insulator, ferromagnetism, and quantum anomalous Hall effects\textsuperscript{11-16}. Numerous theories have been proposed to understand these interesting correlation-induced phases\textsuperscript{17-41}. Very recently, it was also demonstrated that it is possible to realize the correlation-induced phases, which have been observed in the MA-TBG, in non-magic-angle TBG with the twist angle that is slightly larger or smaller than the magic angle\textsuperscript{13,42}. Such a result indicates that the TBG (not limited to the MA-TBG) is a distinctively tunable platform for exploring correlated quantum states. Then, a natural question arises: can we realize new correlation-induced quantum phases in the non-magic-angle TBG, different from that observed in the MA-TBG? A common remarkable property of the TBG with small twist angles lies in that a well-defined and exactly-conserved low-energy degree of freedom, i.e. the valley, emerges. The electron states belonging to the valley $K$ and $K'$ would not be mutually scattered\textsuperscript{7}, leading to the valley U(1)-symmetry. Therefore, it would be very exciting if any new symmetry-breaking phase associated with the special valley degree of freedom is revealed, which is then a new state of matter undiscovered previously.

In this work, we report evidence for a correlation-induced spin and valley polarized metallic phase near the VHS in a non-magic-angle TBG with $\theta \sim 1.49^\circ$ by using high-resolution scanning tunneling microscope and spectroscopy (STM and STS) measurements. The kinetic energy of the quasi-particles around the charge neutrality of the 1.49$^\circ$ TBG is measured to be more than two orders of magnitude smaller than that in the graphene monolayer, which allows to realize correlated phases in this system. When one of the VHSs of the 1.49$^\circ$ TBG is partially filled, we observe substantial broadening of both the two VHSs. Such a behavior is also observed in the MA-TBG
very recently\textsuperscript{43}, indicating that the $e$-$e$ interactions in the 1.49º TBG are still strong. Moreover, the $e$-$e$ interactions split the partially filled VHS of the 1.49º TBG into four peaks, suggesting that both the valley and spin degeneracies of the electron states are lifted. Our analysis based on the continuum model for the 1.49º TBG indicates that the electronic correlation near the VHS will drive a spin and valley polarized metallic phase in which both the valley and spin degeneracies are lifted. Such a spin-valley polarized metallic state belongs to a new symmetry-breaking phase that has not been identified in the MA-TBG or elsewhere previously.

To obtain TBG with a target angle, large-area aligned graphene monolayer was grown on copper foils and the aligned graphene monolayer was cut into two pieces to fabricate TBG with a uniform twist angle\textsuperscript{44,45}. Then, the obtained TBG with controlled $\theta$ was transferred onto a single-crystal Cu substrate covered by an aligned graphene monolayer, as schematically shown in Fig. 1a (see Methods and Supplementary Fig. 1 for the growth of aligned graphene monolayer). The twist angle between the TBG and the supporting graphene monolayer on the single-crystal Cu substrate is larger than 10º to ensure that the TBG is electronically decoupling from the substrate\textsuperscript{4,5,46,47}. Our high-magnetic-field STS measurements observe Landau quantization of the studied TBG, demonstrating explicitly that the TBG is electronically isolated from the substrate. Figure 1b shows a representative STM image of a 1.49º TBG obtained in our experiment, which exhibits a moiré superlattice with the bright (dark) regions corresponding to the AA (AB/BA) stacking region (see Supplementary Fig. 2 for STM images of TBG with different twist angles). The stacking orders in the AA and AB/BA regions are further confirmed in atomic-resolution STM measurements, as shown in Fig. 1c. We obtain a hexagonal-like lattice in the AA region, whereas we obtain a triangular lattice in the AB/BA regions.

There are two main advantages of the studied structure in the STM measurements: (1) it is convenient to obtain large-area TBG with the dimension only limited by the size of the Cu foil; (2) the supporting substrate of the TBG is metallic. In addition, in our experimental setup, the doping of the TBG on the Cu substrate can vary slightly in different areas, which provides a new knob to engineer the novel states compared with
the structure of the TBG on the hexagonal boron nitride (hBN), as studied very recently\textsuperscript{43,48-50}. Figures 1d and 1e show representative STS spectra recorded in two different regions of the 1.49º TBG and the doping in the two regions differs about 30 meV. The slight difference of the doping may arise from variations of the distance between Cu substrate and graphene owning to intercalation of S atoms that segregated from the Cu substrate, as demonstrated very recently\textsuperscript{51,52}. The spectra shown in Figs. 1d and 1e feature two sharp peaks, mainly localized in the AA regions of the moiré pattern, which are the two VHSs of the TBG\textsuperscript{2-5}.

In order to further explore the electronic properties of the 1.49º TBG, we carried out STS measurements in the presence of magnetic fields, as shown in Fig. 2. Figure 2a shows evolution of the STS spectra of the 1.49º TBG as a function of magnetic fields. We can make two obvious observations from these spectra. The first is the appearance of high-energy Landau levels (LLs), as marked by pink arrows, with increasing the magnetic fields. These LLs arise from Landau quantization of the high-energy parabolic bands in the TBG. For simplicity, we can fit these LLs according to the Landau quantization of massive Dirac fermions in Bernal graphene bilayer\textsuperscript{46} and the effective masses for electron and hole are roughly estimated as (0.0168 ± 0.0002)$m_e$ and (0.0158 ± 0.0004)$m_e$, respectively ($m_e$ is free electron mass, see Supplementary Fig. 3 for details of analysis). The second observation is the emergence of LLs of massless Dirac fermions between the two VHSs, as shown in Fig. 2a. To clearly show this, we measured high-resolution STS spectra at 0.4 K as a function of magnetic fields (Fig. 2b) and three LLs of the massless Dirac fermions, 0 and ±1, are observed [the energy resolution is about 5 meV (1 meV) in Fig. 2a (Fig. 2b), see Supplemental materials for details]. By fitting the LLs to Landau quantization of the massless Dirac fermions, we obtain the Fermi velocity as $0.94 \times 10^5$ m/s for electrons and $0.63 \times 10^5$ m/s for holes (see Supplementary Fig. 4 for details). The large electron-hole asymmetry may arise from the enhanced next-nearest hopping in TBG\textsuperscript{4,10}. Obviously, the kinetic energy of the quasi-particles in the 1.49º TBG is strongly suppressed and is more than two orders of magnitude smaller than that in graphene monolayer. As demonstrated very recently\textsuperscript{11-16}, the strongly suppression of the kinetic energy of the quasi-particles is of central role.
in the realization of exotic correlated states in the TBG.

In our experiment, clear evidences for $e$-$e$ correlations are observed in the $1.49^\circ$ TBG. As shown in Figs. 1d and 1e, there is an obvious interaction-enhanced energy separation between the two VHSs $\Delta E_{VHS}$ when the chemical potential is around the charge neutrality of the $1.49^\circ$ TBG. In region II, the right VHS is nearly half filled and the energy separation between the two VHSs is only about 55 meV. In region I, the chemical potential is in between the two VHSs and the $\Delta E_{VHS}$ increases to about 80 meV. Such a result, which has been observed very recently in the MA-TBG\textsuperscript{43,48-50}, indicates that $e$-$e$ interactions should play an important role in determining the electronic properties of the $1.49^\circ$ TBG.

To further explore possible many-body correlations in the $1.49^\circ$ TBG, we carried out high-resolution STS measurements at 0.4 K (the energy resolution is 0.1 meV at 0.4 K, see Supplemental materials for details]. Figure 3 summarizes three representative high-resolution STS spectra recorded in three different regions of the $1.49^\circ$ TBG. The chemical potential is in between the two VHSs in the region I (Fig. 3a), whereas, the chemical potential crosses the right VHS in the region II (Fig. 3b) and region III (Fig. 3c). The doping in the region I and in the region II differs about 30 meV, and the doping in the region II and III differs less than 10 meV. Three notable experimental features can be observed according to the results shown in Fig. 3. The first is the interaction-enhanced $\Delta E_{VHS}$ when the chemical potential is around the charge neutrality of the $1.49^\circ$ TBG, as also revealed in Figs. 1d and 1e. The second feature observed in our experiment is the abrupt broadening of the fully occupied VHS (the left VHS) when the right VHS is partially filled. The full width at half maximum (FWHM) of the fully occupied (the left) VHS is about 25 meV in the region I, however, it increases to about 43 meV (40 meV) in the region II (III) where the right VHS is partially filled. Such a phenomenon is unexpected since that there is no reason to expect a large broadening of the fully occupied bands when the occupation of the other bands is changed. Similar feature is also observed in the MA-TBG and is beyond the description of a weak coupling mean-field picture\textsuperscript{43}. Therefore, this phenomenon is attributed to the experimental evidence that the $e$-$e$ interactions play a dominant role in the MA-TBG\textsuperscript{43}. The above two
experimental features indicate that the effects of e-e interactions are also dominant in the 1.49º TBG even though the twist angle is larger than the magic angle by about 35%. Our result suggests that it is possible to realize strongly correlated phenomena in the TBG with a wide range of twist angle, not limited to the magic angle.

The third and maybe the most notable feature observed in our experiment is the splitting of the positive (the right) VHS into four peaks when that VHS is partially filled, as shown in Fig. 3b and 3c. This one-to-four split of the VHS seems independent of the slight variations of doping between the region II and region III. Such an observation naturally indicates the possibility of the formation of a spin and valley polarized state which lifts up the four-fold spin/valley degeneracy, because the continuum model suggests the existence of an extra valley degeneracy in addition to the spin degeneracy in the TBG. Different from the quantum Hall isospin ferromagnetism state of graphene, no strong magnetic field is needed here and the spin-valley polarization should be purely induced by e-e interactions. Therefore, the four peaks around the Fermi level, as shown in Fig. 3b and 3c, should possibly be attributed to the spin and valley polarized states. Very recently, correlation-induced splitting of the VHSs is also observed in the MA-TBG when the VHS is partially filled. However, the VHS of the MA-TBG only splits into two peaks in the STS measurements. In recent transport measurements, insulating states are observed at all integer occupancies of the eight nearly flat bands in the MA-TBG, with some cases indicating that the four-fold spin/valley degeneracies are fully lifted. However, such spin and valley polarized states have not been detected in previous STM studies on the MA-TBG, which might be influenced by such effects as lattice relaxation, strain, local variation of the twist angle and interlayer coupling. Furthermore, despite the peak splitting, the system should still be in a metallic phase here, as the spectra shown in Fig.3b and 3c suggest large remaining density of state (DOS) on the Fermi level. Such an interaction-driven spin-valley-polarized metallic phase has not been identified previously.

In our experiment, the filling of the 1.49º TBG can also be changed by magnetic fields. As shown in Fig. 2b, more and more states are condensed into the LLs of the massless Dirac fermions with increasing the magnetic fields, which, consequently,
alters the filling of the right VHS. In our experiment, the filling of the right VHS decreases gradually with increasing the magnetic fields for $B > 6$ T. As a consequence, both the broadening of the fully filled VHS (the left VHS) and the splitting of the partially filled VHS (the right VHS) decrease with increasing the magnetic fields. In Fig. 2c, we summarize the FWHM of the fully filled VHS as a function of the magnetic fields. Obviously, it decreases for $B > 6$ T when the filling of the right VHS begins to decrease. According to our experiment, the splitting of the partially filled VHS also depends sensitively on the filling (Fig. 2b). When the right VHS is slightly filled, for example, at $B = 11$ T, the right VHS only splits into two peaks rather than four peaks (see Supplementary Figs. S5 for more data obtained in another region of the 1.49º TBG). These results indicate that the exotic correlated states observed in the TBG should depend sensitively on the filling of the nearly flat bands, as revealed recently in transport measurements\textsuperscript{11-16}.

The splitting of the nearly half-occupied VHS into four peaks can be understood from the spin-valley-polarized order induced by the VHS under $e$-$e$ interactions. To study such order, we start from the continuum-theory band structure\textsuperscript{7} with a twist angle of 1.49º, with proper relax parameters\textsuperscript{19} (see Supplementary Figs. S6-S8 for details). The band structure thus obtained is shown in Fig. 4a. Clearly, four low-energy flat bands (eight flat bands with considering the spin degeneracy) are obtained, which are well separated from the high-energy bands. The nonzero Fermi velocity at the $K_M$ points is $v_F = 1.5 \times 10^5$ m/s and the effective mass of the high-energy parabolic bands is estimated as about $0.02m_e$, which generally agree with that obtained in our experiment. The degeneracies of the high-symmetry points $\Gamma_M$, $M_M$, $K_M$ in the low-energy flat bands of the 1.49º TBG are the same as those of the MA-TBG\textsuperscript{7,19}. The two peaks in the DOS (Fig. 4b), which reproduces the main feature observed in our experiment, are the two VHSs caused by the Lifshitz transition\textsuperscript{23}. Figure 4c shows the Fermi surface (FS) at the VHS in the positive band. From Fig. 4c, the FS-nesting near the VHS is weak, implying less possibility of inducing a density wave (DW) order.

When the system is doped to the VHS, the divergent DOS on the FS will lead to various electron instabilities\textsuperscript{21,40,59-66}, among which the leading one is determined by
the channel in which the largest eigenvalues of the renormalized spin or charge susceptibility matrices \( \chi_{ji}^{(i/e)}(\mathbf{q}, i\omega = 0) \) are the most divergent\(^{23,67-73} \) (see the Supplementary Materials for details). For this purpose, we first calculated the bare susceptibility \( \chi_{ji}^{(0)}(\mathbf{q}, i\omega = 0) \) at the positive VHS doping on a 2000 \( \times \) 2000 lattice. The obtained largest eigenvalue as a function of \( \mathbf{q} \) is shown along the high-symmetry lines in the moiré Brillouin zone in Fig. 4d. Obviously, the highest peak locates at the \( \Gamma_M \)-point which would actually diverge in the thermal-dynamic limit due to the divergent DOS on the FS, implying an electron instability ordered at \( \mathbf{Q} = 0 \).

Furthermore, the eigenvector of the \( \chi^{(0)}(\mathbf{q} = 0, i\omega = 0) \) matrix corresponding to the largest eigenvalue suggests an intra-valley order on the partially-occupied bands. Therefore, up to the zeroth-order perturbation for \( \chi^{(i/e)} \), the induced orders include the intra-valley spin or/and valley polarization. To get more information for the induced orders, we introduce an interacting Hamiltonian which includes a dominating intra-valley scattering term with positive coefficient \( J_z > 0 \) and a minor inter-valley scattering term with coefficient \( J_z \), and perform perturbative treatment for the interactions. The combined three Feynman diagrams for the first-order perturbation of \( \chi_{ji}^{(i/e)}(\mathbf{q}, i\omega) \) shown in Fig. 4e leads to the following results. For \( J_z > 0 \), a pure spin-polarized state is obtained on the partially-occupied band with order parameter in the form of
\[
\Delta^{(s)} \sum_{k\sigma} \sigma (c_{kk\sigma}^+ c_{kk\sigma} + c_{kk\sigma}^+ c_{kk\sigma}^+),
\]
which will split the positive VHS peak into two peaks separated by \( 2\Delta^{(s)} \); for \( J_z < 0 \) a pure valley-polarized state with order parameter
\[
\Delta^{(v)} \sum_{k\sigma} (c_{kk\sigma}^+ c_{kk\sigma} - c_{kk\sigma}^+ c_{kk\sigma}^+)
\]
will be mixed with a locked-spin-valley-polarized state with
\[
\Delta^{(sv)} \sum_{k\sigma} \sigma (c_{kk\sigma}^+ c_{kk\sigma} - c_{kk\sigma}^+ c_{kk\sigma}^+)
\]
on the partially-occupied band, which will split the positive VHS into four peaks separated relatively as \( \pm \Delta^{(v)} \pm \Delta^{(sv)} \).

In the latter case, the electron states represented by each split peak are characterized by a definite spin and valley polarization. This is well consistent with the experimental result. We further carry out a mean-field study for the case with \( J_z < 0 \) (see Supplementary Materials for details), which yields that the two energetically-minimized ground states are just the above obtained two valley-polarized states. The energy difference between the two valley-polarized states is very small (~10\(^{-6} \) meV per unit cell) and therefore they can easily be mixed under perturbations caused by
impurities or the substrate. Such mixing will lead to the unique STS spectrum consistent with our experiments.

Although the spin-valley polarized state obtained here for the 1.49º TBG is induced by the VHS under electron-electron interactions, it differs from the inter-valley spin density wave (SDW) or charge density wave (CDW) states proposed for the MA-TBG\textsuperscript{19,23} due to their different situations of the FS-nesting. In the MA-TBG, the FSs from the valley K and K’ are mutually well nested (see Supplementary Materials for details). This leads to the inter-valley SDW or CDW orders with finite wave vectors, which will generally gap or suppress the VHS peak through band folding and hybridization, leading to a correlated insulator phase. However, the FSs shown here in Fig. 4c are not obviously nested by any vector, which leads to an intra-valley order with \( \vec{Q} = 0 \). Such order will generally split instead of gap the VHS peak, leaving the system metallic. The mechanism for the spin-valley polarization here is similar with the Stoner’s criterion, with the only difference lying in that the extra valley degree of freedom allows for the valley polarization under attractive inter-valley interaction. We note that the VHS here belong to the type II VHS\textsuperscript{74}, which would possibly induce triplet superconductivity upon doping in the absence of FS-nesting. We leave such topic for future study.

In summary, we report evidence for strongly correlation in the 1.49º TBG. When one VHS of the TBG is partially filled, we observe the broadening of the fully occupied VHS and, more importantly, the partially filled VHS splits into four peaks, attributing to the realization of a spin and valley polarized state. Our result indicates that it is possible to realize strongly correlated phases in TBG with a wide range of twist angle and it is also possible to realize new correlation-induced quantum phases, differing from that observed in the magic-angle TBG, in the non-magic-angle TBG.
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Author contributions

Y.R. synthesized the samples, performed the STM experiments, and analyzed the data. C.L., C.C.L. and F.Y. performed the theoretical calculations. L.H. conceived and provided advice on the experiment, analysis, and the theoretical calculation. L.H., Y.R., C.C.L. and F.Y. wrote the paper. All authors participated in the data discussion.

Competing financial interests

The authors declare no competing financial interests.
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FIG. 1. Fabrication and STM characterization of a 1.49° TBG. a. Schematic images showing the fabrication of TBG with controlled twist angle. Aligned graphene monolayer was grown on a copper foil and the as-grown sample was cut into two flakes. Poly (methyl methacrylate) (PMMA) was spin-coated on one of the flakes and the graphene sheet was transferred onto the other one after that the copper foil was etched by ammonium persulfate. Finally, the TGB with controlled twist angle was transferred onto single-crystal Cu covered by graphene monolayer. b. A 25 × 25 nm² STM topographic image (\(V_{\text{sample}} = 60\) mV, \(I = 300\) pA) showing a TBG region with twist angle \(\theta \sim 1.49°\). The periods of moiré lattice in three directions are almost the same with \(L_1 \approx L_2 \approx L_3 = 9.48\pm0.10\) nm. c. The atomic-resolution STM image of red square area in Fig.1a, where the AB/BA stacking regions display triangular graphene lattices, and the AA stacking regions exhibit hexagonal graphene lattices. d and e. Typical \(dI/dV\) spectra recorded at region I and II with different doping of the TBG (a.u. = arbitrary units.). The two peaks around the Fermi level are the two VHSs of the TBG.
FIG. 2. STS spectra of the 1.49º TBG as a function of magnetic fields. a. STS spectra (with 5 meV in energy resolution) as a function of magnetic fields $B$. The high-energy LLs, which arise from the high-energy parabolic-like bands, are marked with pink arrows. The peak between the two VHSs is the zero-LL of massless Dirac fermions. b. High-resolution STS spectra (1 meV in energy resolution) measured in different magnetic fields. The measured energy region corresponds to the grey region in panel a. The LLs of the massless Dirac fermions in the TBG are labeled. c. The FWHM of the fully occupied VHS (the left VHS) as a function of magnetic fields.

FIG. 3. High-resolution tunneling spectra of the 1.49º TBG with different fillings. a-c. Representative STS spectra recorded in the AA region of the 1.49º TBG with different fillings at 0.4 K. In panel a, the Fermi level is in between the two VHSs. In panels b and c, the right VHS is partially filled and the occupations of the right VHS in the region II and III are slightly different. The dashed curves are the fitting of
experimental data, showing that the partial filled VHS splits into four peaks.

**FIG. 4. Theoretical analysis for the VHS-induced instabilities in the 1.49º TBG.**

a. The continuum-theory-based band structure of the 1.49º TBG. b. Density of states of the 1.49º TBG. c. FS of the 1.49º TBG for the VHS doping. The black solid line and red dashed (solid) line in panel a (c) stand for those bands from K and K’ valley, respectively. The dashed hexagon in panel c represents for the moiré Brillouin zone. The small blue circles on the FS denote the Lifshitz-transition points. d. Distribution of the largest eigenvalue of the bare susceptibility matrix along the high-symmetry lines for the VHS doping. e. The three Feynman’s diagrams for the first-order perturbation of the susceptibilities.