Peer Review File

Manuscript Title: Orbital Multiferroicity in Pentalayer Rhombohedral Graphene

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

In this manuscript, the authors have reported a new type of multiferroic order with co-existing valley polarization and orbital magnetization in gate-controlled pentalayer rhombohedral graphene. More importantly, unlike the cases of moire graphene systems and bilayer/trilayer graphene multilayers, the valley polarization and orbital magnetization in this system are decoupled and can be individually controlled using gate electric fields and vertical magnetic fields. The authors demonstrate an electrical switching of orbital magnetization without the necessity of tuning carrier density nor applying in-plane currents. This effect essentially originates from the electric-field switchable Berry curvatures for the holes from a single valley. The authors further investigated the magnetic field and temperature dependence of such magneto-electric effect, then proposed a simple term in the free energy proportional to the product of valley polarization, electric field, and magnetic field, to explain such interesting phenomena. To the best of my knowledge, such a novel type of multiferroic order and the electric-field switchable orbital magnetization have not been reported previously. It is expected to stimulate intensive research on multiferroics, magnetoelectric effects, and 2D materials. The experimental data is comprehensive and convincing, and the theoretical explanation is succinct and clear. Therefore, I would like to recommend this work for publication in Nature given that the authors could properly respond to the following questions and comments.

1. Can we interpret $P=V\cdot B$ as an effective vertical electric polarization which couples linearly with vertical electric field? If so, at fixed (but very small) electric field, switching magnetic field may switch the electric polarization at the cost of $-P\cdot E$. However, switching B at fixed E also switches V, so that the product of the two remains invariant?
Then this is very different from conventional magnetoelectric effect, in which the magnetic-field controlled electric polarization and electric-field controlled magnetization are always concomitant with each other. The authors may elaborate on this point.

2. In Fig. 4e, there is a sudden drop of the critical switching electric field (ET) as a function of temperature. If I understand correctly, ET actually characterizes the temperature evolution of the coupled multiferroic order parameter, which is expected to be a continuous transition across some critical temperature. Where is the sudden jump from? Or it is just because the data in the temperature range 1.5-2K is absent?

3. A minor point: I suggest the authors to draw axes, i.e., vertical axis as energy and horizontal axis as

wavevector k, in the schematics of energy bands in Fig.2d. Since these are 3D plots, it is a bit confusing from which angle one should view these schematics.

Referee #2 (Remarks to the Author):

In the work by Han et al., electric and magnetic fields control of valley and orbital magnetism have been found in moireless rhombohdral pentalayer graphene. The key is the valley-polarized half metal close to zero displacement field in the phase diagram. The experimental results are also well explained by a toy model. Overall, the work is novel and interesting. Hence I recommend its publication in Nature after clarifying some technical issues.

1. Previously it was reported in a thick rhombohderal graphite that the correlated insulating state around E=0 and n=0 responds hysteretically to carrier density and parallel magnetic fields. Similar correlated insulator is also observed in this work. Do they behave in the same way? In particular, is there any response in parallel fields?

2. In Fig. 1a, electron wavefunction is schematically shown to locate at the top and bottom layers, respectively. The ferrovalley order is immediately translated to a ferroelectric order. Can the authors prove the exsitence of such an order?

If it holds, the main ingredients of the theoretical model should include not only the magnetic moment in B fields, thermal energy and the energy barrier, but also the electrostatic energy (as a function of electric fields). This may change the g-factor derived in Fig. 4.

3. The phase diagram in extended Fig.1 is labeled by various flavor polarization, but without any evidence (except the studied VPHM). Is there any more information to verify the other phases?

4. The magnetic moment is expected to depend on carrier density as well as electric fields. n=-0.55E12 cm^-2 and -0.67E12 cm^-2 have been shown in the main text and extended Fig. 9, respectively. The g-factors for the latter and some other densities are suggested to be derived from the above figures, so that one may gain a through understanding of how the magnetic moments develops with varying carrier density (i.e., the berry curvature distribution).

Referee #3 (Remarks to the Author):

The authors studied the low temperature electronic transport in dual-gated rhombohedral 5-layer graphene device. In the flat valence band, they observe spontaneous valley isospin polarization in a ‘bubble’ region around zero electric field. This polarization is evidenced by an anomalous Hall signal, owing to the opposite Berry Curvature in K and K’ valleys and quantum oscillations in parts of the bubble which show a reduced degeneracy. Rxy in the same parts of bubble region show hysteretic behavior. Hysteresis in the electric field takes on a butterfly like shape, which can be explained by

ferro-valleytricity, as the authors call it. They demonstrate independent control of the valley and orbital magnetic order changing only the electric field.

The current work is novel in the ways the authors describe in the paper, by demonstrating independent control of valley and orbital magnetization. From a basic science perspective the demonstration of a new type of ferroic order will be exciting to a wide range of condensed matter physicists. The question of relevance and interest to a wider audience is a hard one even for papers that clearly belong in Nature. I believe the importance of this work is on par with other recent graphene-based works published in Nature. However, I believe the authors can do a better job justifying the importance of the work to a broader audience, specifically in the abstract and introduction by expanding on the "great promise for applications and many theory proposals" mentioned.

While the overall logic and conclusions of the paper appear sound to me, at some points the presentation of the data is confusing or lacking. Specifically,

• The false-color plots in Fig. 2. are very low quality (in the photo quality sense), jpeg artifacting is evident making it difficult to view subtle features in the data. The quantum oscillations in Fig. 2b are very hard to see. I suggest either a line cut showing the oscillations or a more appropriate colormap to make the oscillations more apparent. It was only after looking at the supplements that I was able to see the features the authors' were referring to.
• In Fig. 5c, there is no way to discern from the plot what the applied electric field in the regions where switching occurs is. There is only a vertical line to indicate some change in the field before returning to its steady value.
• The clarity of this portion would be greatly enhanced by a schematic showing why the path of the electric field in 5b leads to either valley or magnetic switching. In the same vein, there is no attempt in the text to explain why these routes through the butterfly lead to the observed effects.

Additionally, I would also like to see the inclusion of Raman spectra showing the rhombohedral nature of the device and evidence that the flake maintained it's stacking order after its incorporation into the device.

Other minor points:

In the abstract, line 16 "orders are driven purely by the orbital degrees of freedom but electron spin", I believe should read ", but not electron spin".

Line 63 "in nature crystals" should read "in natural crystals", I presume.

Fig 2b. g=2 annotation is not explained in figure caption and not referenced directly in the text. Further, the use of g to describe the degeneracy could confuse the reader as later in the paper g refers to the g-factor.

Fig. 2e caption should specify in words what delta Rxy is and how it is extracted should be included in the text.

Fig. 4c,d. Arrows pointing to the extracted E_B and E_T values would be useful. Especially at higher fields in c, it is not necessarily clear where one would mark the ‘butterfly ending’

“The value of M cannot be measured directly due to the small size of our device” is technically incorrect, magnetism is such devices can be imaged and quantified using scanned probe magnetometry for example. I understand why the authors did not perform this experiment, but more precise language is required.

Author Rebuttals to Initial Comments:

Responses to the referees

We sincerely thank the referees for taking the time to assess our manuscript and raising suggestions to improve it. We believe that this letter and the revised manuscript fully addressed their technical questions and comments. In the following, we respond in detail to the questions and comments that were raised one by one. Throughout this letter we used the Italic and bold style for the questions by the referees and the standard style for our responses. Changes made in the revised manuscript are highlighted in yellow.

Referee #1 (Remarks to the Author):

In this manuscript, the authors have reported a new type of multiferroic order with co-existing valley polarization and orbital magnetization in gate-controlled pentalayer rhombohedral graphene. More importantly, unlike the cases of moire graphene systems and bilayer/trilayer graphene multilayers, the valley polarization and orbital magnetization in this system are decoupled and can be individually controlled using gate electric fields and vertical magnetic fields. The authors demonstrate an electrical switching of orbital magnetization without the necessity of tuning carrier density nor applying in-plane currents. This effect essentially originates from the electric-field switchable Berry curvatures for the holes from a single valley. The authors further investigated the magnetic field and temperature dependence of such magneto-electric effect, then proposed a simple term in the free energy proportional to the product of valley polarization, electric field, and magnetic field, to explain such interesting phenomena. To the best of my knowledge, such a novel type of multiferroic order and the electric-field switchable orbital magnetization have not been reported previously. It is expected to stimulate intensive research on multiferroics, magnetoelectric effects, and 2D materials. The experimental data is comprehensive and convincing, and the theoretical explanation is succinct and clear. Therefore, I would like to recommend this work for publication in Nature given that the authors could properly respond to the following questions and comments.

We thank Referee #1 for appreciating the quality and merits of our manuscript by summarizing the main points, comparing it with existing literatures, and pointing to further directions for improvement.

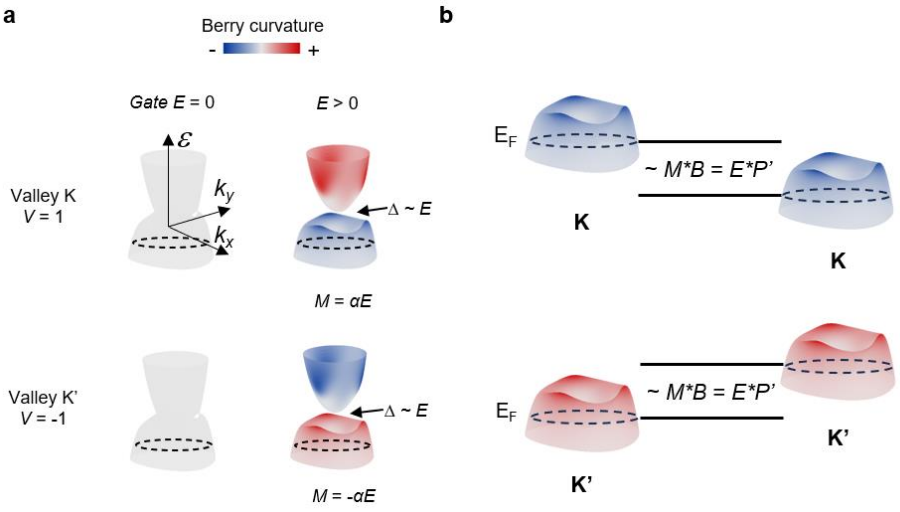
1. Can we interpret P=V·B as an effective vertical electric polarization which couples linearly with vertical electric field?

Yes, the free energy relevant for the ferro-valleytricity can be viewed as $F = - E*(\alpha V*B)$, where $(\alpha V*B)$ is an effective electric dipole that couples to the gate electric field E. We will call this dipole as P' in the following.

We note that the total electric polarization/dipole has two parts. Without considering the valley symmetry breaking, an electric dipole is induced by the gate electric field E. At gate electric field E = 0 mV/nm, in both K and K' valleys, both the conduction and valence band wave functions have 50% at the top layer and 50% at the bottom layer, preserving the inversion symmetry of the lattice structure; when a non-zero E is applied, the inversion symmetry is broken so in both valleys the valence-band-wave-function is polarized in the layer with a lower potential energy while the conduction-band-wave-function is polarized in the opposite layer. From the band structure point of view, applying a gate electric field opens up the band gap proportional to E and lowers the energy of the valence band, as shown in R Figure 1a. The total energy lowering of the valence band and occupied states is equivalent to an electrostatic energy of $E*P_0$, where the electric dipole P_0 is induced by the applied E and characterizes the number of electrons whose energy is

affected by the gap opening. P_0 and E^*P_0 do not depend on valley polarization, so it does not contribute to the free energy when we consider the orbital magnetism and ferro-valleytricity.

When the valley symmetry is spontaneously broken in the presence of a magnetic field B, the bands in K and K' valley shift in energy due to the coupling between the orbital magnetization and B. This coupling results in the free energy $F = -\alpha E^*V^*B = -(\alpha E^*V)^*B$, where αE^*V is the averaged orbital magnetic moment as we stated in the manuscript. This same energy can be viewed as $F = -E^*(\alpha V^*B)$, where (αV^*B) is an effective electric dipole P'. This additional electric dipole P' is determined by both V and B, and it is involved in the ferro-valleytricity behavior. From the band structure point of view, this electric dipole and the corresponding electrostatic energy can be seen from the shift of the occupied states in valence band in a magnetic field B, as shown in R Figure 1b.

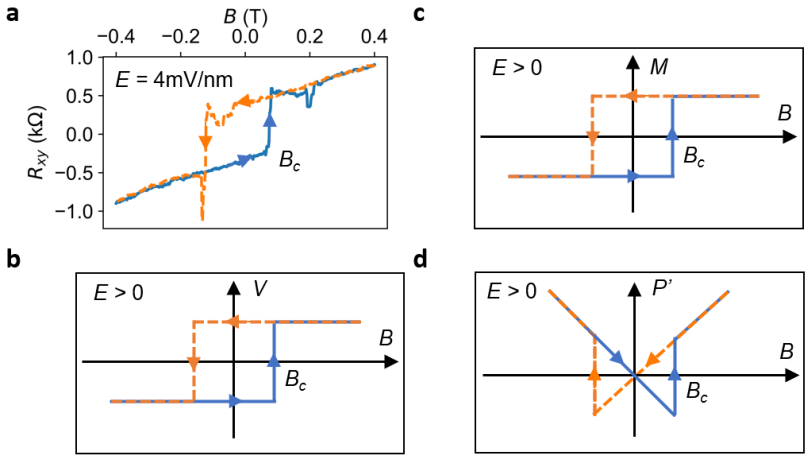


R Figure 1. Illustration of electrical dipoles in pentalayer graphene. a. The opening of the band gap by a gate electric field E is effectively inducing an electric dipole P_0 which couples to E and lowering the energy of the occupied states. The Berry curvature and orbital magnetization in the K and K' valleys are opposite. **b.** Given a non-zero E, the valence bands in the K and K' valley experience further shift in a magnetic field B. The shift is proportional to the orbital magnetization of the occupied states. This shift in energy $M^*B = \alpha E^*B$ can be viewed as $M^*B = E^*(\alpha B) = E^*P'$, where is effectively an additional electric dipole P'. This latter part of electric dipole P' matters for the valleytricity while the P_0 does not.

If so, at fixed (but very small) electric field, switching magnetic field may switch the electric polarization at the cost of -P·E. However, switching B at fixed E also switches V, so that the product of the two remains invariant?

This is partially correct. Given the discussion above, we now focus on P'. It is true that switching magnetic field will immediately switch the electric polarization as $P' = \alpha V^*B$, but V remains the same until one reaches the coercive magnetic field B_c. After reaching the coercive magnetic field, V will also switch so that the product of V and B remains invariant. The energy cost $-E^*P'$ during the hysteresis as pointed out by the referee is actually exactly (up to a factor of 2) the energy difference $2M^*B$ between states (K, $-M$) and (K', $+M$) shown in Fig. 4. This can be seen as $2E^*P' = 2\alpha V^*E^*B = 2M^*B$, where $P' = \alpha V^*B$ and $M =$

αV^*E. No matter one scans E or B, this energy cost is the same. To help visualize the hysteresis process, here we plot the hysteresis loops versus B and explicitly label the V, the M and P' as R Figure 2.



R Figure 2. Magnetic field hysteresis of *V*, *M* and *P'*. a. R_{xy} versus magnetic field B taken at E = 4mV/nm (same data in Fig. 2d). Clear anomalous Hall and hysteresis is observed. B_c is the critical field where the switching happens. **b-d.** The corresponding valley polarization (V), orbital magnetic moment (M) and effective electric polarization (P') as a function of B.

Then this is very different from conventional magnetoelectric effect, in which the magnetic-field controlled electric polarization and electric-field controlled magnetization are always concomitant with each other. The authors may elaborate on this point.

Before reaching E_c, the linear part of the butterfly hysteresis of R_{xy} could be viewed as conventional magnetoelectric effect where the free energy $F = -\alpha V^*B^*E = -E^*P' = -B^*M$. Beyond E_c or B_c, the valley polarization is switched. In another word, the valley polarization V can be viewed as the coefficient of conventional magnetoelectric effect, which usually can be controlled through strain in conventional multiferroic or magneto-electrics, for example.

We feel this is an excellent question that deserves clarification and we have included our response above in the Supplementary Materials of the revised manuscript.

2. In Fig. 4e, there is a sudden drop of the critical switching electric field (ET) as a function of temperature. If I understand correctly, ET actually characterizes the temperature evolution of the coupled multiferroic order parameter, which is expected to be a continuous transition across some critical temperature. Where is the sudden jump from? Or it is just because the data in the temperature range 1.5-2K is absent?

This is a great point and we agree that E_T should go to zero continuously as the temperature approaches the critical temperature. The sudden jump is indeed due to a difficulty of collecting data at 1.5-2 K. In our He-4 VTI setup, the lowest sample temperature one can get is 2 K, by pumping He-4. In the dilution refrigerators, it is hard to stabilize the sample temperature in the range of 1.5-2 K due to the evaporation

and boiling of the He3/He4 mixture. Therefore, we are not able to experimentally extract E_T in this range of temperature.

When extracting the *g*-factor, we used values of E_T by linear interpolation in this range. Despite not being ideal, we think it is acceptable given the technical difficulty in the experiment and the small range of parameters that affect our data analysis. To make sure that readers understand this subtle detail, we have included the following text in the Extended Data section.

'The absence data at 1.5-2 K in Fig. 4e is due to the difficulty of stabilizing the sample temperature in this range in our experimental setups. When extracting the *g*-factor, we used values of E_T by linear interpolation in this range.'

3. A minor point: I suggest the authors to draw axes, i.e., vertical axis as energy and horizontal axis as wavevector k, in the schematics of energy bands in Fig.2d. Since these are 3D plots, it is a bit confusing from which angle one should view these schematics.

We thank the referee for this suggestion. We have followed it and modified Fig. 2d accordingly.

Referee #2 (Remarks to the Author):

In the work by Han et al., electric and magnetic fields control of valley and orbital magnetism have been found in moireless rhombohdral pentalayer graphene. The key is the valley-polarized half metal close to zero displacement field in the phase diagram. The experimental results are also well explained by a toy model. Overall, the work is novel and interesting. Hence I recommend its publication in Nature after clarifying some technical issues.

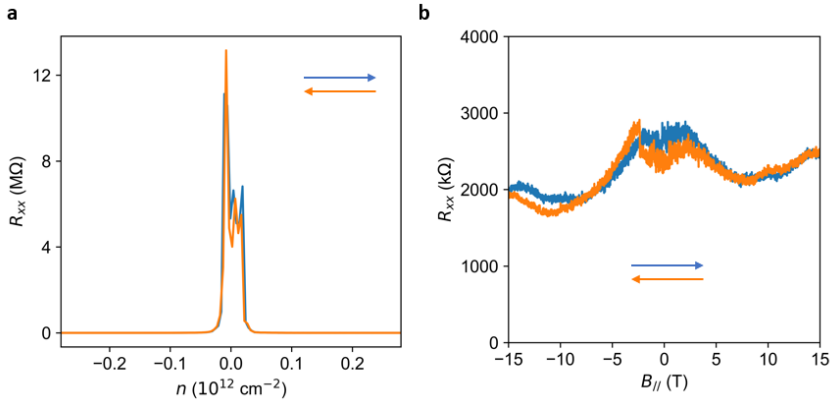
We thank Referee #2 for appreciating the novelty and quality of our manuscript.

1. Previously it was reported in a thick rhombohderal graphite that the correlated insulating state around E=0 and n=0 responds hysteretically to carrier density and parallel magnetic fields. Similar correlated insulator is also observed in this work. Do they behave in the same way? In particular, is there any response in parallel fields?

We thank this referee for raising up this question. We have performed similar measurements as in the reference *Nature* 584 (7820), 210-214[1] on our pentalayer graphene device and here we show our data. Within in the range of +-15 T (which is the safe limit of the superconducting magnet in SCM1 at the National High Magnetic Field Laboratory in Tallahasse, FL, USA), the forward and backward scans do not overlap, but we do not see a clear hysteresis as reported in *Nature* 584 (7820), 210-214. Here we provide our understanding of this difference:

1. In *Nature* 584 (7820), 210-214, the authors claimed that their device 'have insulating electronic phases that are separated into domains'. In our pentalayer graphene, the magnetic hysteresis shows mainly a single jump in R_{xy} and the valley hysteresis shows only two states (butterfly or 'M'). These observations seem to suggest a largely uniformly distributed property, instead of phase separations.
2. The resistance of the correlated insulating state we observed is about three orders of magnitude higher than that in *Nature* 584 (7820), 210-214. It is possible that the correlation effect is more

robust in pentalayer graphene than in the thicker layers of rhombohedral graphene. So even if there is hysteresis versus $B_{//}$ in pentalayer graphene, it might take a much bigger value of $B_{//}$ than 15 T to reveal the hysteresis, as the hysteresis in *Nature* 584 (7820), 210-214 happens when the correlated insulating state is killed by large enough $B_{//}$.



R Figure 3. Density and in-plane magnetic field scan at E = 0. a, R_{xx} versus forward and backward scanning of n. **b.** R_{xx} versus forward and backward scanning of $B_{//}$.

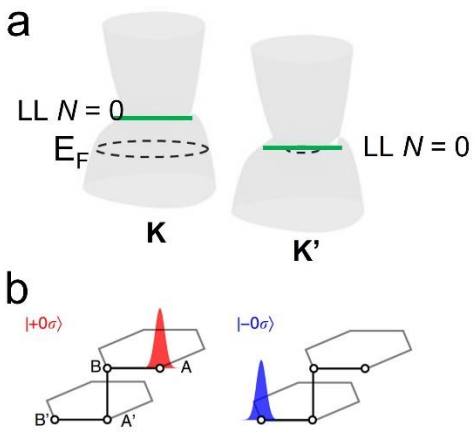
2. In Fig. 1a, electron wavefunction is schematically shown to locate at the top and bottom layers, respectively. The ferrovalley order is immediately translated to a ferroelectric order. Can the authors prove the exsitence of such an order?

We agree with the referee that the existence of ferroelectric order is an important question. But before answering that question, we would like to clarify on the colors used in Fig. 1. We are not sure if this happened to this referee, but we realized that there might be some confusion about the correspondence between layers and conduction/valence bands, due to the same blue-red color-schemes we used for Fig. 1a (representing the top and bottom layers) and Fig. 1b (representing the conduction and valence bands). We thank the referee for giving us a chance to eliminate the confusion. In the revised manuscript, we have changed the colors of the top and bottom layers in Fig. 1a from blue and red to green and orange.

Based on the corrected Figure 1, we explain the relation between layer polarization (which corresponds to electric dipole) and valley polarization. Please see our reply to the question #1 raised by Referee #1 for the explanation of the two effective electric dipole P_0 and P'. Basically, at gate electric field E = 0 mV/nm, in both K and K' valleys, both the conduction and valence band wave functions have 50% at the top layer and 50% at the bottom layer, yielding a zero layer-polarization and electric dipole. When a non-zero E is applied, the inversion symmetry is broken and an electric dipole P_0 is induced by E. So P_0 is unrelated to valley polarization. Vice versa, the ferro-valley order does not imply a ferro-electric order, since the system can have a big(small) Fermi surface in the K(K') valley even if the symmetry between the top and bottom layers of rhombohedral graphene is preserved, as shown by the states at the center of the butterfly in Fig. 3c of the original manuscript.

When the valley symmetry is spontaneously broken and a magnetic field B is applied, there is an effective electric dipole $P' = \alpha V^*B$ originating from the free energy $F = -\alpha V^*B^*E$. In the presence of B, P' (at E = 0 mV/nm) and valley polarization V should indeed co-exist. Here we provide a physical picture to

understand this (R Figure 4). At a non-zero *B*, electron states form discrete Landau levels. Taking the zeroth Landau level as an example (other Landau levels have qualitatively similar sublattice and layer polarization, but quantitatively not as big as that in the zeroth Landau level), its electron wavefunctions in the K and K' valleys are located at the A and B sublattices respectively. In all rhombohedral graphene, A and B sublattices to describe the lowest-energy bands are located at the top and bottom layers. Therefore, a valley polarization leads to the imbalance of population of the zeroth Landau level, which results in a layer polarization of electric charge distribution and electric dipole.



R Figure 4. Ferro-electricity in the valley-polarized state at *E* = 0, |*B*| > 0. a. Illustration of the valley polarization and imbalanced population of the zeroth Landau levels in K and K' valley at a non-zero *B*. **b.** Valley and sublattice and layer has a one-to-one-to-one correspondence in the zeroth Landau level of rhombohedral graphene. Thus a valley polarization at non-zero B implies layer polarization and an electric dipole at *E* = 0 mV/nm. In this picture, ferro-electricity should exist at *E* = 0 mV/nm and |*B*| > 0 mT**.** Panel **b** is adapted from *Nature Communications* 8.1 (2017): 948[2].

However, we do not have direct evidence of a non-zero electric dipole through direct measurements. To properly address this issue, a sensing layer (such as a monolayer graphene as the top gate in *Nature* 560, 336–339 (2018)[3]) or a layer-sensitive measurement (such as capacitance measurements as in *Nature Communications* 12, 5298 (2021)[4]) have been demonstrated as effective experimental schemes. But these experiments require a different device configuration and a significantly different measurement scheme from those in our manuscript. Especially, replacing the top gate by a monolayer graphene will require a completely new device that is hard to make due to the fragile nature of the rhombohedral pentalayer graphene. We hope that we can eventually explore the possibility of ferro-electricity in pentalayer graphene, after the fabrication of rhombohedral pentalayer graphene is improved to have higher yield. But for now, the demonstration of ferro-electricity is not the point we are trying to make within this story: the two different types of ferroic orders and hysteresis already support our main conclusion of orbital multi-ferroics.

If it holds, the main ingredients of the theoretical model should include not only the magnetic moment in B fields, thermal energy and the energy barrier, but also the electrostatic energy (as a function of electric fields). This may change the g-factor derived in Fig. 4.

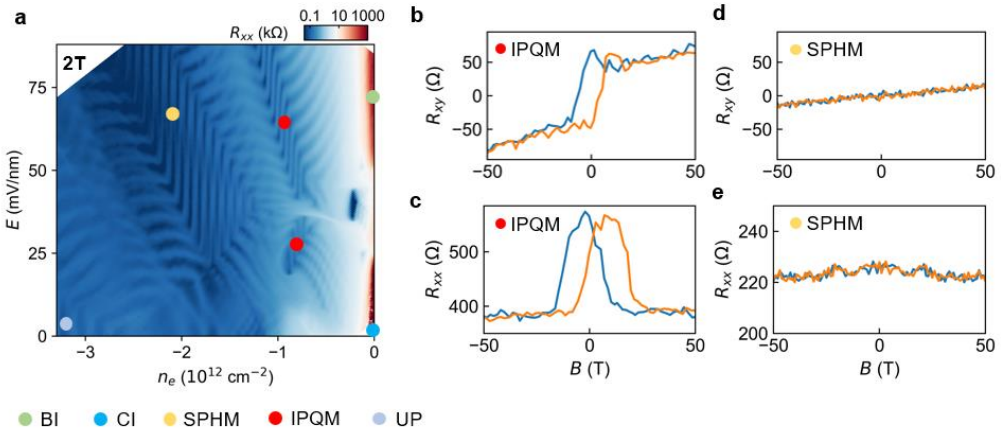
As explained above, there are indeed two electrostatic energies and they are already properly considered in our model. The first energy is $-E*P_0$, which is already accounted by the shift of valence bands to lower the energy at non-zero *E*. This energy does not depend on the valley polarization so it is not relevant for the discussion of ferro-valleytricity and ferro-magnetism. The second electrostatic energy is $-E*P'=-\alpha V*B*E$ which is exactly the free energy we have considered in our original manuscript. In our manuscript we described it as $-B*M$ where $M = \alpha V*E$. We should not count the same energy twice so we did not explicitly discuss the equivalence between $E*P'$ and $B*M$.

To clarify on this and help the readers to understand it, we have included the discussion above and R Figure 4 in the Supplementary Materials in our revised manuscript.

3. The phase diagram in extended Fig.1 is labeled by various flavor polarization, but without any evidence (except the studied VPHM). Is there any more information to verify the other phases?

We thank the referee for raising this question, which helps to clarify the big phase diagram of pentalayer graphene. The isospin-polarized states except for the VPHM are not related to the physics we discuss in the current manuscript, so we did not show more data about them. We are happy to provide the quantum oscillation and anomalous Hall data of those states here, which can also be seen from another manuscript we placed on arXiv as arXiv:2305.03151[5]. We include them here for the referee's reference. In the revised manuscript, we have included the following sentence in the Extended Fig.1 Caption so readers can get these data from the arXiv manuscript.

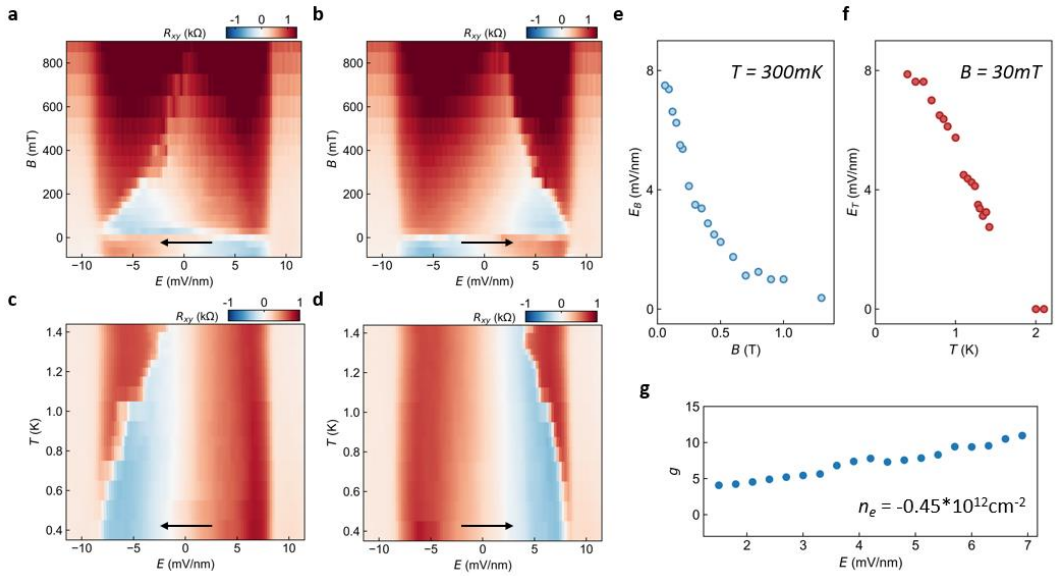
'The details of IPQM and SPHM states can be found in arXiv:2305.03151.'



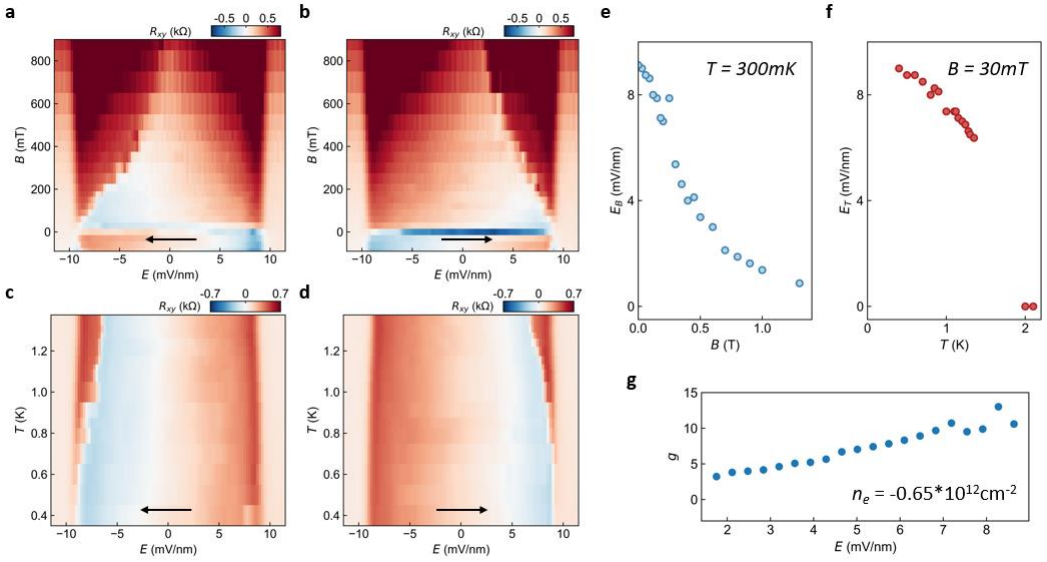
R Figure 5. Phase diagram of rhombohedral pentalayer graphene. a. R_{xx} as a function of carrier density n and electric field E measured at B = 2T. Colored dots label different phases including band insulator (BI), correlated insulator (CI), spin-polarized half metal (SPHM), isospin-polarized quarter metal (IPQM) and unpolarized metal (UP). The Landau level spacing indicates the Fermi surface degeneracy. **b, c**. Hall resistance R_{xy} and longitudinal resistance R_{xx} as a function of the out-of-plane magnetic field at the red dot (IPQM) in **a**. **d, e**, R_{xy} and R_{xx} at the yellow dot (SPHM) in **a**. The quarter metal **b** & **c** shows a clear anomalous Hall effect and magnetic hysteresis, indicating a net valley polarization. While the half metal **d** & **e** does not show anomalous Hall effect or magnetic hysteresis, indicating the absence of net valley polarization. Therefore, we conclude the half metal to be spin polarized but not valley unpolarized.

4. The magnetic moment is expected to depend on carrier density as well as electric fields. n=-0.55E12 cm^-2 and -0.67E12 cm^-2 have been shown in the main text and extended Fig. 9, respectively. The g-factors for the latter and some other densities are suggested to be derived from the above figures, so that one may gain a through understanding of how the magnetic moments develops with varying carrier density (i.e., the berry curvature distribution).

We agree with the referee that measuring the *g*-factor as a function of carrier density and electric fields in the whole range of 'wings' would be ideal. Besides data at n = -0.55*10^{12} cm^{-2}, we performed more measurements and include here the data at n = -0.45*10^{12} cm^{-2} and n =-0.65*10^{12} cm^{-2}.



R Figure 6. Evolution of the 'butterfly' as a function of magnetic field and temperature at n_e = -0.45*10^{12} cm^{-2}. a & b. R_{xy} as E is scanned at different magnetic fields. **d.** R_{xy} as E is scanned at different temperatures and B = 30 mT. **e & f.** Critical fields E_B and E_T extracted from **a**-**d**. **g.** Effective g-factor of the averaged orbital magnetic moment as a function of E extracted from **e & f**.



R Figure 7. Evolution of the 'butterfly' as a function of magnetic field and temperature at n_e = -0.65*10^{12} cm^{-2}. a & b. R_{xy} as E is scanned at different magnetic fields. **d.** R_{xy} as E is scanned at different temperatures and B = 30 mT. **e & f.** Critical fields E_B and E_T extracted from **a**-**d**. **g.** Effective g-factor of the averaged orbital magnetic moment as a function of E extracted from **e & f**.

We note that such measurements (E_B and E_T as a function of magnetic field and temperature) are very time-consuming, and we have very limited time in dilution refrigerators (especially the SCM1 at the National High Magnetic Field Laboratory in Tallahassee, FL, USA). Therefore, we are not able to provide more data at other charge densities at this moment (and even in several months). We hope the referee could understand this. Scientifically, we believe the original data in our manuscript and the new data at n =-0.45*10^{12} cm^{-2} and n =-0.65*10^{12} cm^{-2} are already representative enough of the observations, and they provide a good starting point for theoretical modeling of the underlying physics. We have included R Figure 6 & 7 as Extended Fig. 7 in our revised manuscript.

Referee #3 (Remarks to the Author):

The authors studied the low temperature electronic transport in dual-gated rhombohedral 5-layer graphene device. In the flat valence band, they observe spontaneous valley isospin polarization in a 'bubble' region around zero electric field. This polarization is evidenced by an anomalous Hall signal, owing to the opposite Berry Curvature in K and K' valleys and quantum oscillations in parts of the bubble which show a reduced degeneracy. Rxy in the same parts of bubble region show hysteretic behavior. Hysteresis in the electric field takes on a butterfly like shape, which can be explained by ferro-valleytricity, as the authors call it. They demonstrate independent control of the valley and orbital magnetic order changing only the electric field.

The current work is novel in the ways the authors describe in the paper, by demonstrating independent control of valley and orbital magnetization. From a basic science perspective the demonstration of a new type of ferroic order will be exciting to a wide range of condensed matter physicists. The question of relevance and interest to a wider audience is a hard one even for papers that clearly belong in Nature. I believe the importance of this work is on par with other recent graphene-based works published in Nature. However, I believe the authors can do a better job justifying the importance of the work to a broader audience, specifically in the abstract and introduction by expanding on the "great promise for applications and many theory proposals" mentioned.

We thank Referee #3 for appreciating the novelty of our manuscript and its potential importance to a broader audience. To address the concern on justifying the importance of the work to a broader audience, we have added/revised the following text in the abstract and introduction

'Such orbital multiferroics could offer strong valley-magnetic couplings and large responses to external fields---enabling device applications such as multiple-state memory elements, as well as electric field control of valley and magnetic states.'

'For example, information could be stored in multiple states with different combinations of valley and magnetic characters instead of being limited to the binary states of spin. Furthermore, such multiple states can be manipulated conveniently by an electric field.'

'Despite its great promise for applications and many theory proposals of realizing multiferroics in heterostructures of graphene and transition metal dichalcogenides, an orbital multiferroics with independent switching of the valley order and the orbital magnetism have remained elusive.'

While the overall logic and conclusions of the paper appear sound to me, at some points the presentation of the data is confusing or lacking. Specifically,

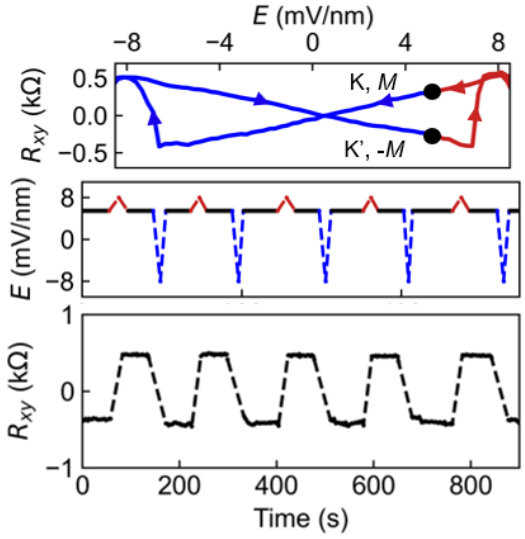
• The false-color plots in Fig. 2. are very low quality (in the photo quality sense), jpeg artifacting is evident making it difficult to view subtle features in the data. The quantum oscillations in Fig. 2b are very hard to see. I suggest either a line cut showing the oscillations or a more appropriate colormap to make the oscillations more apparent. It was only after looking at the supplements that I was able to see the features the authors' were referring to.

We have followed the referee's suggestion by changing a better colormap to make the quantum oscillation more apparent.

• In Fig. 5c, there is no way to discern from the plot what the applied electric field in the regions where switching occurs is. There is only a vertical line to indicate some change in the field before returning to its steady value.

This is a good point and we thank the referee for giving us the opportunity to make this part clearer and to correct for a small error. The previous version of Fig. 5c only shows the static states to serve the purpose of showing non-volatile switching. Now we revise Fig. 5c by showing the complete process of the switching. We also add a schematic of the path along the butterfly to clarify how the switching is achieved, as shown in R Figure 8. In the same spirit, we also add the schematics in Fig. 5b as will be discussed in the next question.

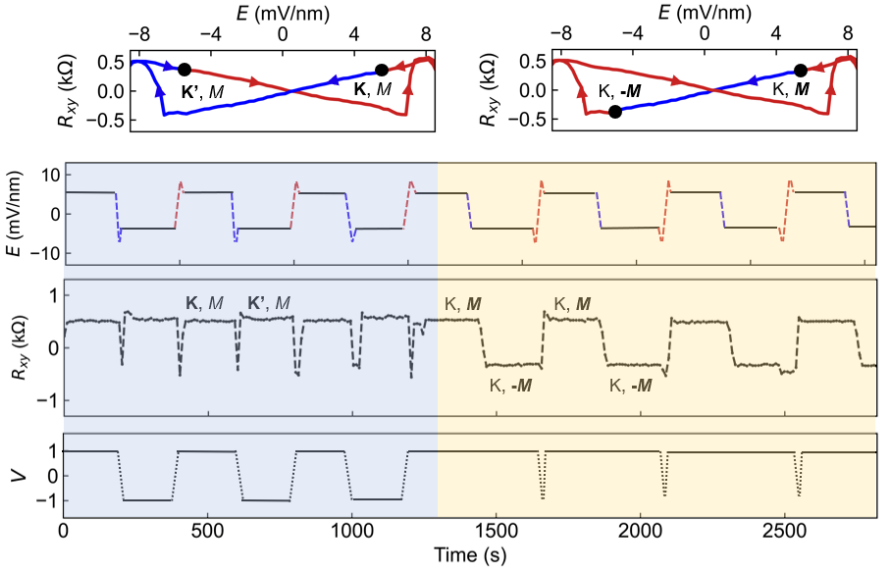
The top panel shows the path of switching along the butterfly. The two dots mark the two static states (K, *M*) and (K', -*M*). The red and blue paths depict the switching process between the two states, and the arrows label the scanning direction. The color of the two switching paths corresponds to the color of the switching pulse in the middle panel. We have replaced Fig. 5c by R Figure 8 in our revised manuscript.



R Figure 8. Non-volatile switching of orbital magnetism and valley polarization using electric field. The top panel shows the path of switching between the two static states (K, *M*) and (K', -*M*) labeled by the two dots. The color of the two switching paths corresponds to the switching pulse in the middle panel and the arrows indicate the scanning direction. The lower panel shows the measured R_{xy} corresponding to the electric pulse sequence.

• The clarity of this portion would be greatly enhanced by a schematic showing why the path of the electric field in 5b leads to either valley or magnetic switching. In the same vein, there is no attempt in the text to explain why these routes through the butterfly lead to the observed effects.

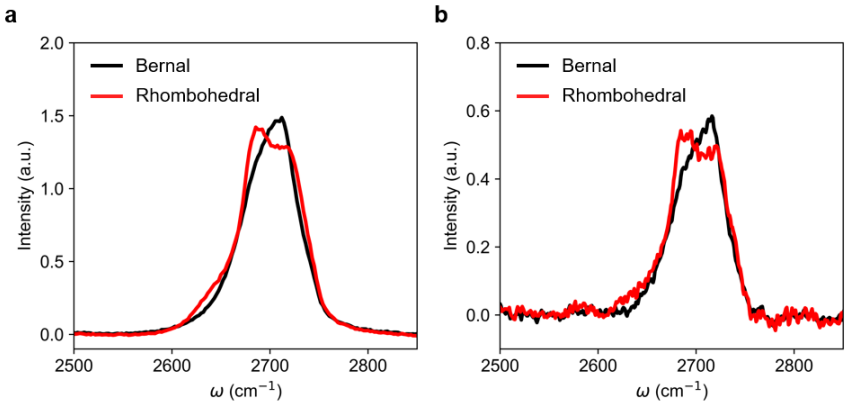
We have followed the referee's suggestion and included the butterfly in Fig. 5b so the readers can see the switching of valley and magnetization on-spot. As shown in R Figure 9, we have labeled the traces along the butterfly that leads to the switchings, and highlighted the states at the steady values of E in the same way as R Figure 8. The two panels on the top describe the paths to realize independent switching of the valley V and orbital magnetic moment M respectively. We have replaced Fig. 5b by R Figure 9 in our revised manuscript.



R Figure 9. Independent switching of the valley and orbital magnetism. The two panels on the top describe the path along the butterfly to switch the valley (left, blue-shaded region) and orbital magnetic moment (right, yellow-shaded region) respectively. We label the traces of the switching in the same way as in R Figure 8.

Additionally, I would also like to see the inclusion of Raman spectra showing the rhombohedral nature of the device and evidence that the flake maintained it's stacking order after its incorporation into the device.

We have included the Raman spectra of the pentalayer graphene flake before pickup and after fully encapsulated by hBN in the Supplementary materials. All spectra show the 2D peak features corresponding to the rhombohedral stacking order.



R Figure 10. Raman spectra of the flake before and after hBN encapsulation. a, b, 2D Raman peak of Bernal (black) and rhombohedral (red) stacked pentalayer graphene before (**a**) and after (**b**) hBN encapsulation. The rhombohedral stacking is preserved after hBN encapsulation.

Other minor points:

In the abstract, line 16 "orders are driven purely by the orbital degrees of freedom but electron spin", I believe should read ", but not electron spin".

We have corrected for this typo by changing the text to 'but not electron spin'.

Line 63 "in nature crystals" should read "in natural crystals", I presume.

We have corrected for this typo by changing the text to 'in natural crystals'.

Fig 2b. g=2 annotation is not explained in figure caption and not referenced directly in the text. Further, the use of g to describe the degeneracy could confuse the reader as later in the paper g refers to the g-factor.

We thank the referee for raising this important conflict of notation. To address it, we have changed 'g' to 'd' for representing the degeneracy, and explained it in the figure caption as 'the period in density corresponds to two isospin flavors (degeneracy $d = 2$) at the Fermi level'.

Fig. 2e caption should specify in words what delta Rxy is and how it is extracted should be included in the text.

We have added in the figure caption 'ΔR_{xy} is the amplitude of the abrupt jump of the transverse resistance'. To explain how ΔR_{xy} is extracted, we have added in the text 'which is extracted by averaging the changes of R_{xy} at the two vertical edges of the magnetic hysteresis loop'.

Fig. 4c,d. Arrows pointing to the extracted E_B and E_T values would be useful. Especially at higher fields in c, it is not necessarily clear where one would mark the 'butterfly ending'

We have followed this suggestion by adding arrows to point to the extracted E_B and E_T in Fig. 4c & d.

"The value of M cannot be measured directly due to the small size of our device" is technically incorrect, magnetism is such devices can be imaged and quantified using scanned probe magnetometry for example. I understand why the authors did not perform this experiment, but more precise language is required.

We appreciate the referee's valuable suggestion. In the revised manuscript, we have modified this sentence as 'The value of M is hard to be measured directly through transport measurements, due to the small size of our device'.

References

1. Shi, Y. *et al.* Electronic phase separation in multilayer rhombohedral graphite. *Nature 2020 584:7820* **584**, 210–214 (2020).

2. Hunt, B. M. *et al.* Direct measurement of discrete valley and orbital quantum numbers in bilayer graphene. *Nature Communications 2017 8:1* **8**, 1–7 (2017).

3. Fei, Z. *et al.* Ferroelectric switching of a two-dimensional metal. *Nature 2018 560:7718* **560**, 336–339 (2018).

4. de la Barrera, S. C. *et al.* Direct measurement of ferroelectric polarization in a tunable semimetal. *Nature Communications 2021 12:1* **12**, 1–9 (2021).

5. Han, T. *et al.* Correlated Insulator and Chern Insulators in Pentalayer Rhombohedral Stacked Graphene. *arXiv preprint arXiv:2305.03151* (2023).

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

The authors have properly responded to all my questions and comments. Now I recommend this work for publication in Nature.

Referee #2 (Remarks to the Author):

The four questions in the last round could be grouped into three:

1. (Q3) With the help of the arXiv paper from the same authors, the phase diagram of a pentalayer r-graphene become clear and convincing.

2. (Q1) The nature of the insulating ground state at D=0, n=0 remains unclear. From R Figure 3, one can see the almost unchanged resistance in parallel fields, in line with the observation in a tetralayer r-graphene posted recently on arXiv. Such a B// dependence seems to contradict the scenario of a spin polarized insulator that was claimed in the tetralayer r-graphene. The nature of this correlated insulator needs to be further investigated.

I understand this is not the main topic of this manuscript. Nevertheless, the R Figure 3 is suggested to be added in supplementary files, as an evidence for establishing a theoretical model in the future.

3. (Q2&Q4) The main concern is the nature of multiferroic transition driven by electric and magnetic fields, which is also pointed out by Referee #1. After going through the response, the picture seems more confusing.

The key is whether valley and layer are interlocked. Two scenarios are poosible:

(a) In the reply to Q2, they are assumed to be locked, analogous to the quantum Hall ferromagnetism (R Figure 4). Then my proposal of charge polarization in the last round is reasonable. Take Fig. 3c in the main text as an example, we can see the competition between electromagnetic energy and valley exchange energy: (a) Starting from the left and top corner (blue curve), the K' valley is populated by holes that reside in the bottom layer to lower the potential energy for E<0. (b) Increasing E along the blue curve to a positive value, the potential energy of electric dipoles increases. Concomitantly, the magnetic moment changes sign so that the magnetic energy also increases (and possibly, much more significantly). (c) When the sum of the two energies exceeds the energy barrier (\delta in Fig. 4f in the main text) caused by the valley exchange interaction, the valley changes from K' to K.

If the above reasoning is valid, for sure the g factor needs to be updated.

(b) However, in the reply to Referee #1, the authors think there is no interlock between layer and valley by stating that 'when a non-zero E is applied, the inversion symmetry is broken so in both valleys the valence-band-wave-function is polarized in the layer with a lower potential energy while the conduction-band-wave-function is polarized in the opposite layer' and 'the ferro-valley order does not imply a ferro-electric order, since the system can have a big(small) Fermi surface in the K(K') valley even if the symmetry between the top and bottom layers of rhombohedral graphene is preserved'. So, the energy comptition of Fig. 3c is between magnetic energy and valley exchange interaction. This reasoning is also possible, if one assumes the magnetic moment is in linear relationship with the electric field (including both magnitude and sign).

In such a scenario, the claim is propably not proper that there is an effective dipole derived from the free energy formula. Anyway, it seems to be NOT straightforward why a transition from K' to K valley - without layer-valley locking - will reduce the electric potential energy.

4. In R Figure 1a, \delta is assigned to the correlation gap between conduction and valence bands. Is this \delta the same with the one in Fig. 4f?

5. In the revised manuscript, the authors tried to derive an effective dipole from the free energy to support the concept of multiferroicity. This is not necessary, as the unique valleyferroicity is interesting by itself. Even if the valley and layer are locked, the valley-ferroicity is distinct from a convention multiferroicity, because in the former (again, take Fig. 3c as an example) the mechanism of valley switching driven by an electric field is mainly due to the magnetic energy rather than electrostatic potential in the latter.

Overall, the model supporting the nice experimental results is suggested to be refined.

Referee #3 (Remarks to the Author):

In my opinion, the authors have very thoroughly responded to all referee comments and the manuscript is suitable for publication in Nature.

Author Rebuttals to First Revision:

Responses to the referees

We sincerely thank the referees for taking the time to assess our manuscript and raising suggestions to improve it. We believe that this letter and the revised manuscript fully addressed their technical questions and comments. In the following, we respond in detail to the questions and comments that were raised one by one. Throughout this letter we used the Italic and bold style for the questions by the referees and the standard style for our responses. Changes made in the revised manuscript are highlighted in yellow.

Referee #1 (Remarks to the Author):

The authors have properly responded to all my questions and comments. Now I recommend this work for publication in Nature.

We thank Referee #1 for the thoughtful questions/comments in the first round of review and recommendation of our work.

Referee #2 (Remarks to the Author):

The four questions in the last round could be grouped into three:

1. (Q3) With the help of the arXiv paper from the same authors, the phase diagram of a pentalayer r-graphene become clear and convincing.

We thank Referee #2 for appreciating our arXiv paper, which discusses physics that is orthogonal to this manuscript under consideration at Nature.

2. (Q1) The nature of the insulating ground state at D=0, n=0 remains unclear. From R Figure 3, one can see the almost unchanged resistance in parallel fields, in line with the observation in a tetralayer r-graphene posted recently on arXiv. Such a B// dependence seems to contradict the scenario of a spin polarized insulator that was claimed in the tetralayer r-graphene. The nature of this correlated insulator needs to be further investigated.

We are aware of the arXiv paper on tetralayer r-graphene. However, the observation, the interpretation and specific claim made by that paper is irrelevant to our manuscript under consideration at Nature.

We agree that the state at $D = 0$ and $n = 0$ deserves further investigation, and there could be similarity and/or difference between tetralayer and pentalayer. We are indeed trying other spectroscopy measurement techniques to investigate this state. Given the suggestion by this referee, we are more encouraged to do so as its significance has been pointed out by this referee.

I understand this is not the main topic of this manuscript. Nevertheless, the R Figure 3 is suggested to be added in supplementary files, as an evidence for establishing a theoretical model in the future.

We have followed the referee's suggestion by including R Figure 3 as Fig. S4 to the supplementary files of our revised manuscript. We have also added a note to refer to our arXiv paper for the discussion of the general phase diagram of pentalayer r-graphene.

The details of IPQM and SPHM states can be found in ref [56].

56. Han, T. *et al.* Correlated Insulator and Chern Insulators in Pentalayer Rhombohedral Stacked Graphene. *arXiv preprint arXiv:2305.03151* (2023).

3. (Q2&Q4) The main concern is the nature of multiferroic transition driven by electric and magnetic fields, which is also pointed out by Referee #1. After going through the response, the picture seems more confusing.

We appreciate the referee's question and we are happy to explain it. It was not clear to us exactly what was the referee's picture in mind in the previous round. With the more detailed comments below by the referee, we now understand exactly what the concern was, and we will address it correspondingly below.

The key is whether valley and layer are interlocked.

We acknowledge that this is the key question, and its answer has two parts. Firstly, when $B = 0$, the valley and layer are not interlocked. The only electric dipole in the system is the trivial gate-induced electric dipole P_0. This dipole exists in any rhombohedral graphene with layer number $N > 2$ when the layer symmetry is broken by a gate electric field, as a band gap can be opened due to the low-energy wave-function is located at the top and bottom layers of rhomboheral graphene. It is a pure single-particle effect and the layer polarization is completely unrelated to the valley polarization: no matter which valley is occupied, the layer polarization does not change as it is determined by the applied E, as we explained in the reply to Reviewer #1.

Secondly, when $B \neq 0$, there is an induced layer polarization and electric dipole $P' = \alpha V^* B$, in addition to P_0. As P' is proportional to V, this additional layer polarization and electric dipole is locked with the valley polarization. This is analogous to the quantum Hall ferromagnetism case as Reviewer #2 pointed out. The coupling of P' with E leads to the free-energy we specified as $F = -E^* P' = -E^*(\alpha V^* B)$. As we explained in last round's response, this energy is relevant to the ferro-valleytricity. Although it can be viewed as a magnetic energy $F = -B^* M = -B^*(\alpha V^* E)$, the quantum Hall ferromagnetism picture backs up the interpretation of the same energy as electric dipole P' coupled to E. We think the referee #2 and us already share the same understanding of the quantum Hall ferromagnetism picture of this P'.

Two scenarios are possible:

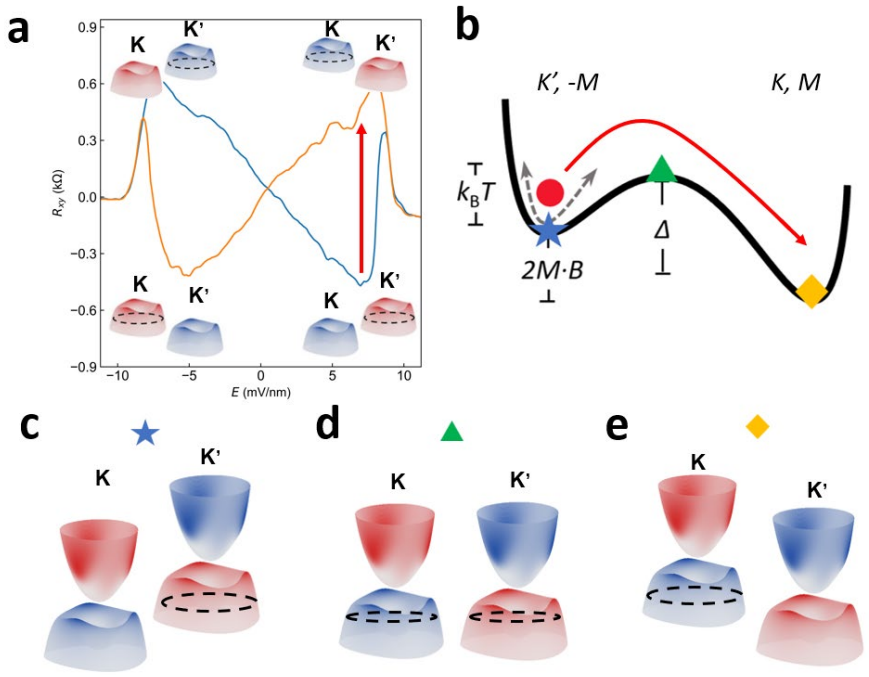
(a) In the reply to Q2, they are assumed to be locked, analogous to the quantum Hall ferromagnetism (R Figure 4).

Q2 was about electric dipole in general, and our reply made it clear that there are two electric dipoles, P_0 and P'. The former does not depend on valley polarization because the band gap opening by electric field applies to both valleys. The latter does depend on valley polarization V as $P' = \alpha V^* B$. R Figure 4 was to explain the physical picture of how to understand the microscopic origin of P', because P_0 is zero at $E = 0$

mV/nm and the total electric dipole is simply P'. At E = 0 mV/nm and a non-zero B, we agree with the referee that the system could be thought of as a quantum Hall ferromagnet, although the magnetic field we applied is way below the value at which clear discrete Landau levels are separated from each other (which corresponds to a quantum Hall ferromagnet). In this case, there is a valley-layer locking when we consider only P'.

Then my proposal of charge polarization in the last round is reasonable. Take Fig. 3c in the main text as an example, we can see the competition between electromagnetic energy and valley exchange energy: (a) Starting from the left and top corner (blue curve), the K' valley is populated by holes that reside in the bottom layer to lower the potential energy for E<0. (b) Increasing E along the blue curve to a positive value, the potential energy of electric dipoles increases. Concomitantly, the magnetic moment changes sign so that the magnetic energy also increases (and possibly, much more significantly). (c) When the sum of the two energies exceeds the energy barrier (\delta in Fig. 4f in the main text) caused by the valley exchange interaction, the valley changes from K' to K.

We thank the referee for bringing up this scenario, as it helps us understand exactly where the confusion was. We agree on the step (a) and (b) as described by the referee in general, but would like to clarify on the electric potential energy, as this is where the confusion might have happened. Specifically, the potential energy of electric dipoles is $-E*(P_0+P')$, including both dipoles. Although the electric potential energy includes a term that is $-E*P_0$, we note that this energy should not be counted in the flipping process from K' to K: as we explained above, P_0 is unrelated to valley polarization, so **all the states on the free-energy curve in Fig. 4f have exactly the same potential energy $-E*P_0$ as they correspond to the same E and P_0 is unrelated to valley polarization. This is really the key point that could solve all the confusions, we believe.** As a result, in step (c), the only energy to consider in the fight with the energy barrier Δ (valley exchange interaction) is $-E*P' = -E*(\alpha V*B) = -B*(\alpha V*E) = -B*M$, which is exactly what we considered in our initial modeling and extraction of the g-factor. At elevated temperatures, the thermal energy k_BT will assist the flipping which happens at $\Delta = -B*M + k_BT$. To help understand this, we illustrate the band structure and the valley-dependent Fermi surface corresponding to Fig. 4f, as shown in R Figure 1. No matter what the valley polarization (corresponding to different states on the free energy curve of the valley 'magnet') is, the band gap of both K and K' valleys are fixed by the gate electric field E. Therefore the electric potential energy $-E*P_0$ does not contribute to overcoming the valley-exchange energy barrier, although $-E*P_0$ does change when scanning E. In another word, the only effect of E in the flipping process is to change the orbital magnetization (so that the valley-exchange energy can be overcome by $-B*M$) but not directly overcoming Δ by electric potential energy.



R Figure 1. Illustration of the electric field-induced flipping of valley polarization. a. The butterfly hysteresis featuring four different valley-polarized states. At a positive gate electric field E, the system flips from K' valley to K valley as indicated by the red arrow. **b.** The free-energy plot corresponding to the flipping process as indicated by the red arrow in **a,** where the blue star, green triangle and yellow diamond correspond to states polarized in K' valley, valley-unpolarized, and polarized in K valley. **c-e.** Illustrations of the band structure and Fermi surface in the three states highlighted in **b**. Although these three states have different valley polarizations, the band gap induced by the gate electric field does not depend on valley polarization. Therefore the electric dipole energy $-E^*P_0$ is a constant for all states in **b**, and this energy does not contribute to overcome the energy barrier (valley-exchange interaction energy) Δ.

If the above reasoning is valid, for sure the g factor needs to be updated.

As we explained above, although the overall picture is correct, the *g*-factor we extracted was proper and does not need to be updated.

(b) However, in the reply to Referee #1, the authors think there is no interlock between layer and valley by stating that 'when a non-zero E is applied, the inversion symmetry is broken so in both valleys the valence-band-wave-function is polarized in the layer with a lower potential energy while the conduction-band-wave-function is polarized in the opposite layer' and 'the ferro-valley order does not imply a ferro-electric order, since the system can have a big(small) Fermi surface in the K(K') valley even if the symmetry between the top and bottom layers of rhombohedral graphene is preserved'.

As we explained above, these statements were referring to the electric dipole energy $-E^*P_0$, but not to $-E^*P'$. P' does correspond to the interlock between layer and valley.

So, the energy competition of Fig. 3c is between magnetic energy and valley exchange interaction. This reasoning is also possible, if one assumes the magnetic moment is in linear relationship with the electric field (including both magnitude and sign).

As we explained above when discussing about step (c), the energy competition of Fig. 3c is between the valley exchange interaction and energy $-E*P' = -E*(\alpha V*B) = -B*(\alpha V*E) = -B*M$, which is the magnetic energy as the referee called, but is equivalent to and can be interpreted as the electric dipole energy of a quantum Hall ferromagnet. We totally agree with the referee's comment '***the energy competition of Fig. 3c is between magnetic energy and valley exchange interaction***'.

In such a scenario, the claim is propably not proper that there is an effective dipole derived from the free energy formula.

With the explains above, we believe that the two scenarios outlined by the referee #2 are essentially the same scenario, if we realize that the magnetic energy is equivalent to the electric dipole energy $-E*P' = -E*(\alpha V*B) = -B*(\alpha V*E) = -B*M$, and realize that the other electric dipole energy $-E*P_0$ does not contribute to the flipping from valley K' to K.

Anyway, it seems to be NOT straightforward why a transition from K' to K valley - without layer-valley locking - will reduce the electric potential energy.

Again, the transition from K' to K valley does flip the sign of P' and the corresponding electric potential energy. Although the referee tends to interpret this energy as the magnetic energy, it can also be thought of as the electric potential energy in a quantum Hall ferromagnet picture. We believe that the referee was confused because: 1. the referee thinks $-E*P_0$ is the only electric dipole energy while $F = -E*(\alpha V*B)$ is a magnetic energy; 2. we think $F = -E*(\alpha V*B)$ can be viewed as a magnetic energy or electric dipole energy, equivalently; 3. we did not explain clearly enough that the electric potential energy $-E*P_0$ does not contribute to the flipping process. We think the referee's comment did help us identify where the confusion was, and we hope our explanation above made it clear. To help readers to understand the picture from different angles, we have included the discussion to this question in the Supplementary Materials of the revised manuscript.

4. In R Figure 1a, \delta is assigned to the correlation gap between conduction and valence bands. Is this \delta the same with the one in Fig. 4f?

The 'Δ' in R Figure 1a is the gate-induced gap, as we explicitly explained in the figure caption which says 'a. The opening of the band gap by a gate electric field E'. This gap is not the correlation gap, and we have never mentioned the correlation gap in this manuscript.

The 'Δ' in Fig. 4f means the energy barrier in the free-energy picture. We explicitly said in the figure caption 'The flipping happens when the magnetic energy $M \bullet B$ and thermal energy k_BT add up to overcome the energy barrier 'Δ'.

These two symbols refer to different physical quantities, as explained above. R Figure 1a was added to the Supplementary Materials of the last version of manuscript. We understand that this could cause confusions, so we have changed the symbol for the gate-induced gap from 'Δ' to 'E_0', and modified the text, figures

and figure captions in the main text, the extended figures and supplementary materials accordingly. We thank the referee for raising this possibly confusing point.

5. In the revised manuscript, the authors tried to derive an effective dipole from the free energy to support the concept of multiferroicity. This is not necessary, as the unique valleyferroicity is interesting by itself.

We thank the referee for the consistent appreciation of the significance of our experimental observation of valley-ferroicity (ferro-valleytricity). Our effort on explaining the effective dipole was to provide a view from another angle, to help the referees and readers to understand the phenomenon.

Even if the valley and layer are locked, the valley-ferroicity is distinct from a convention multiferroicity, because in the former (again, take Fig. 3c as an example) the mechanism of valley switching driven by an electric field is mainly due to the magnetic energy rather than electrostatic potential in the latter.

We agree that the mechanism of valley-ferroicity (ferro-valleytricity) is distinct from a conventional multiferroicity, and the valley switching driven by an electric field is due to the magnetic energy. This is the reason for which we do not think an extra electrostatic energy should be included, when answering the question/comment 2 of this referee in the last round, and as we explained above in the discussion of question/comment 3 in this round, which says ***'If it holds, the main ingredients of the theoretical model should include not only the magnetic momentin B fields, thermal energyand the energy barrier, but also the electrostatic energy (as a function ofelectric fields). This may change the g-factor derived in Fig. 4.'***

Overall, the model supporting the nice experimental results is suggested to be refined.

We understand that this comment is related to the referee's comment 3 at above. As we explained there, we think the model is reasonable and consistent with the experimental observation. We hope that including the discussions above in our revised manuscript could help clarifying the picture. We agree that it would be nice if our work triggers both experimental and theoretical efforts to study ferro-valleytricity and orbital multi-ferroicity in two-dimensional materials. But we feel that would be beyond the scope of our current manuscript.

Referee #3 (Remarks to the Author):

In my opinion, the authors have very thoroughly responded to all referee comments and the manuscript is suitable for publication in Nature.

We thank Referee #3 for the thoughtful questions/comments in the first round of review and recommendation of our work.

Reviewer Reports on the Second Revision:

Referees' comments:

Referee #2 (Remarks to the Author):

The response has clarified the concerns about valley- and charge-polarization. And I realize that the LAF ground state is indeed a reasonable picture. Now I recommend this manuscript for publication in Nature.