

Spectroscopic evidence for a first-order transition to a possible orbital Fulde-Ferrell-Larkin-Ovchinnikov state

Corresponding Author: Professor Ding Zhang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors performed tunneling spectroscopy measurements on NbSe₂ thin film. They observed a sudden enhancement of the superconducting gap near a critical field B_0 that is below B_{c2} , where the transition line possibly marks the first-order transition from the uniform Ising SC and orb-FFLO. They also studied the temperature and thickness dependence of the phase diagram.

Previously, there were several experimental papers that presented the transport study of orb-FFLO in layered TMD. However, the first-order transition from the uniform Ising SC to orb-FFLO is not easy to map out solely from transport measurement, despite being theoretically known. This work fills the gap via tunneling spectroscopy, which could detect the pairing gap size. To my knowledge, this work is the first experimental work that gives clear experimental signatures of such first-order transition via tunneling spectroscopy. I think this work is a timely and important work for the exploration of orb-FFLO in layered TMD. Therefore, I recommend the publication of this work in Nature Communications.

I have a few comments and questions for the authors, which I think need to be addressed before final publication:

1. I would expect that the gap is discontinuous across the transition due to first-order transition. But this is not clear to me in Fig. 1g, although I can see a sudden increase near B_0 . The authors should discuss the reason.
2. It is a concern to me that if Josephson vortex lattice appears in the phase diagram, it may mimic the signature of orb-FFLO in tunneling spectroscopy, such as modulating the gap and giving hysteresis, etc. Previously, in layered organic superconductor [Phys. Rev. B 100, 014515 (2019)], the interlayer resistance versus in-plane magnetic field shows a similar in-plane hysteresis behavior as the dI/dV measurement in Figure 2 of this paper. In [Phys. Rev. B 100, 014515 (2019)], Josephson vortex lattice seems to play a role in giving rise to such hysteresis. The authors should figure out where or whether Josephson vortices phase appears in the phase diagram as well.
3. Regarding the results shown in Fig. 3, what is the phase region above orb-FFLO region (SC-2) but below B_{c2} ? Why does the B_{c2} seem to increase for thicker sample, which is counterintuitive?
4. "Due to the increasing energy cost in the uniform Ising superconducting state, a thicker sample therefore tends to transition to the orb-FFLO state at a lower field." It is unclear to me why thicker sample requires lower field to realize orb-FFLO, and the change of onset field is so dramatic from 20nm to 30nm thick sample in Figure3. As long as interlayer coupling is weak, I would not expect a significant difference between bilayer and multilayers. Can the authors explain their claim more clearly?
5. "Our theoretical fitting indicates that the 30 nm thick NbSe₂ hosts such a modulation in the a-b plane with a period of about 1.6 μm at an in-plane magnetic field around 1 T, inviting future spatial imaging studies under much less demanding conditions." In the theoretical calculation, the authors assumed FFLO pairing in each layer so that there are even gap modulation within each layer? By the way, in the theoretical part, the authors put the momentum of Cooper pairs in the top half number of layers to be positive q , while bottom half number of layers to be negative q . But this configuration setting looks different from the one considered in previous Justin Ye's Nature paper, where the Cooper pair momentum is opposite in between two nearest layers.

Reviewer #2

(Remarks to the Author)

The manuscript entitled "Spectroscopic evidence for a first-order transition to a possible orbital Fulde-Ferrell-Larkin-Ovchinnikov state" by Cao et al. reports tunneling spectroscopy measurements that reveal a first-order phase transition associated with the orbital FFLO state. There are few experimental reports on this topic, and if the observed behavior is intrinsic, it provides strong support for the existence of the orbital FFLO state. Data are nicely shown and the results will be of great interest not only to the people in 2D materials community but also to those in the superconductivity community. I therefore recommend publication in Nature Communications. Below are several minor comments that should be addressed before publication.

1. In Fig. 4, D is defined as the sample thickness, while in line 331, D is named as the interlayer spacing, which is very confusing. In addition, as for $N = D/\xi_c$ in line 398, if D corresponds to the sample thickness, this implies that NbSe₂ layers within the ξ_c are regarded as a single layer in the Lawrence–Doniach model. Is this correct? The situation of the orbital FFLO is not sufficiently clear and a schematic illustration would be helpful for readers.

2. Is there any physical reason why the superconducting gap becomes larger in the orbital FFLO phase? In addition, if the tunnel junction size were made to be smaller than the domain size of FFLO phase, would the observed step-like behavior disappear?

3. Naturally, we expect (B^*, T^*) to coincide with (B_3, T_3) . Is there any physical reason why they differ in the present results?

4. In the Methods section, authors mentioned that h-BN is etched using CF₄/O₂. Does this process cause oxidization or degradation of the sample? Could sample degradation or resulting inhomogeneity be an alternative explanation for the observed behavior?

5. There are few typos:

Line 201: "dependenc" → "dependence"

Line 336: "superconconutor" → "superconductor"

Reviewer #3

(Remarks to the Author)

This manuscript reports a systematic transport and spectroscopic study of NbSe₂ flakes with thickness in the 10-30 nm range, aiming to probe the thermodynamic signature of the transition from a uniform Ising superconducting state to the proposed orbital FFLO (orb-FFLO) state induced by an in-plane magnetic field. Using resistance and tunnel spectroscopy measurements, the authors first identify the phase space for the orb-FFLO by confirming the upturn in the field-temperature dependence reported in the literature. Using tunnel spectroscopy based on NbSe₂/WS₂/graphite heterostructures, they observe clear hysteretic changes in the conductance at both zero bias and at the bias corresponding to the coherence peak, consistent with a first-order transition. This behavior is shown to be extremely sensitive to field orientation, appearing only within less than one degree of the in-plane direction. The authors further show that similar behavior can be observed in the closely related NbS₂, but is absent in FeSe, arguing against this being a generic feature of multiband superconductors. On the theory side, they show that the orb-FFLO can be favored in relatively thicker samples over the Ising superconducting state with a uniform order parameter. Moreover, the phase space in the field-temperature phase diagram expands as the sample thickness increases. The calculated phase diagram is in quantitative agreement with the experimental results.

The study of unconventional superconductivity such as the FFLO phase is of central importance in condensed matter physics, and the recently proposed orb-FFLO phase has attracted increasing interest. The observation of thermodynamic evidence for a field-driven transition into this phase is a significant advance, as most previous reports relied on resistance measurements alone and spectroscopic information has been lacking. In this sense, the present work provides more concrete evidence that this phase may indeed exist, and it enables a more reliable determination of the phase diagram because the first-order transition is more clearly revealed. The experiments are well designed and carefully executed, and the manuscript is clearly written, combining theory with careful discussion of alternative scenarios. Overall, I find this work to be of high quality and likely to become an important reference for the field. I have a few issues that I hope the authors can address to further strengthen the manuscript.

Can the authors further clarify their physical understanding of the orb-FFLO? Specifically, the Discussion mentions vortex formation. Do Abrikosov vortices form within the theoretical framework used for the orb-FFLO here? If yes, how do they interact with, or modify, the orb-FFLO state? If not, why are vortices not expected? Relatedly, how should one understand the effects of disorder on the orb-FFLO?

The authors propose that phase transitions occurring in multiple domains are responsible for the hysteresis observed in the differential conductance as a function of magnetic field. If this is the case, should one also expect hysteresis in resistance versus field measurements? If not, please clarify why the domain scenario would produce a pronounced hysteresis in

tunneling conductance but not in transport.

In the Methods, some important experimental details appear to be missing, which are essential for reproducibility by other groups. The authors should explain why WS₂ was chosen as the tunneling barrier. Given possible interfacial charge transfer between WS₂ and NbSe₂, could unusual phenomena arise from the specific properties of this interface, which complicate the interpretation? What thickness of WS₂ was used to optimize the quality of the tunnel spectroscopy data? The device schematic in Figure 1 indicates a trilayer WS₂. Was this tested to be the optimal thickness? Would hexagonal BN be a better choice?

Also in this section, two different techniques for differential conductance measurements are introduced, but detailed description is provided only for the current-bias case. Since most samples were measured using the voltage-bias method, the details of that method should be included as well. It is also stated that a four-terminal configuration was used. How exactly were the four terminals wired and used in the two types of measurement? A wiring schematic would be helpful for interested readers.

In Table 1, the extracted spin-orbit coupling energy scale for sample S2 is much larger than that for the other samples. A possible explanation should be provided.

Supplementary Figure 5 shows data for sample S4 measured at mK temperatures. The caption states that the color shading indicates the orb-FFLO and the uniform Ising superconducting state (Ising-SC), but it is unclear how these phases map onto panel c. In panel e, the field-induced change in differential conductance across the first-order transition is less pronounced than that observed at higher temperatures, for example at 1.6 K in Figure 1 for sample S2. Why does the signature of the first-order transition weaken at such low temperature, where thermal broadening is reduced?

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have done a great job addressing my comments and improving their manuscript. I now strongly recommend the publication of this version in Nature Communications.

Reviewer #2

(Remarks to the Author)

The authors have properly addressed the reviewer's comments and questions. The revisions have significantly improved the clarity of the manuscript. Therefore, I recommend this paper for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The authors have addressed all my questions. I recommend the publication of this manuscript in Nature Communications.

Open Access This Peer Review File is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

In cases where reviewers are anonymous, credit should be given to 'Anonymous Referee' and the source.

The images or other third party material in this Peer Review File are included in the article's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this license, visit <https://creativecommons.org/licenses/by/4.0/>

Reviewer #1 (Remarks to the Author):

The authors performed tunneling spectroscopy measurements on NbSe₂ thin film. They observed a sudden enhancement of the superconducting gap near a critical field B_0 that is below B_{c2} , where the transition line possibly marks the first-order transition from the uniform Ising SC and orb-FFLO. They also studied the temperature and thickness dependence of the phase diagram.

Previously, there were several experimental papers that presented the transport study of orb-FFLO in layered TMD. However, the first-order transition from the uniform Ising SC to orb-FFLO is not easy to map out solely from transport measurement, despite being theoretically known. This work fills the gap via tunneling spectroscopy, which could detect the pairing gap size. To my knowledge, this work is the first experimental work that gives clear experimental signatures of such first-order transition via tunneling spectroscopy. I think this work is a timely and important work for the exploration of orb-FFLO in layered TMD. Therefore, I recommend the publication of this work in Nature Communications.

[Our response] We would like to thank the reviewer for recommending our work for publication. We also appreciate the high recognition of the reviewer on the importance of our work.

I have a few comments and questions for the authors, which I think need to be addressed before final publication:

1. I would expect that the gap is discontinuous across the transition due to first-order transition. But this is not clear to me in Fig. 1g, although I can see a sudden increase near B_0 . The authors should discuss the reason.

[Our response] The reviewer is correct that the first-order transition should ideally behave as a discontinuous jump. In our experiment, we found that the first-order transition sensitively depends on the orientation of the magnetic field and the disorder. In case of the data shown in Fig. 1, it is due to the slight misalignment of the magnetic field that the transition looks smeared. Similar smoothening of the transition appears in Fig. 2a/b. In Fig. 2d, however, the transition indeed shows the discontinuous jumps at 0° . This is because we further fine-tuned the orientation of the magnetic field. Figure 2d also indicates that the transition becomes smoothened and less pronounced at 0.2° . Judging from this evolution, we reason that the angle for obtaining the data in Fig. 1e, f and Fig. 2a, b is between 0° and 0.2° . We add the following statement in the main text to discuss this point: “the data in Fig. 1e,f and Fig. 2a,b may have been taken with a slight misalignment of about 0.1° .”

2. It is a concern to me that if Josephson vortex lattice appears in the phase diagram, it may mimic the signature of orb-FFLO in tunneling spectroscopy, such as modulating the gap and giving hysteresis, etc. Previously, in layered organic superconductor [Phys. Rev. B 100, 014515 (2019)], the interlayer resistance versus in-plane magnetic field shows a similar in-plane hysteresis behavior as the dI/dV measurement in Figure 2 of this paper. In [Phys. Rev. B 100, 014515 (2019)], Josephson vortex lattice seems to play a role in giving rise to such hysteresis. The authors should figure out where or whether Josephson vortices phase appears in the phase diagram as well.

[Our response] We thank the reviewer for raising this possibility and listing the helpful reference. Indeed, vortices should be present in our sample. However, as demonstrated by the listed reference, the hysteretic behavior occurred once the vortex lattice got de-pinned. This depinning gave rise to finite interlayer resistance. Similar resistance under an in-plane magnetic field is expected to occur in our NbSe₂ samples once the vortices get de-pinned (*Phys. Rev. B* **46**, 6395 (1992)). In contrast, we experimentally observe only zero resistance around B_0 , as shown in Supplementary Figs. 3b, 5b, 8b. We therefore reason that the vortex lattice stays pinned within the temperature and magnetic field range that we study. The number of vortices increases with the in-plane magnetic field continuously and does not generate any sudden change in the energetics. We have added the following descriptions in the discussion section together with the reference suggested by the reviewer (cited as ref. 40):

“We also exclude the depinning of vortices or the melting of vortex lattice⁴⁰ as the mechanism for the observed sudden change, because they would give rise to magneto-resistance. By contrast, the resistance stays zero around B_0 in our experiment.”

We have also added the following statement in the theoretical note of the Methods:

“Although vortices can enter our samples, they serve as a background and do not generate any sudden change in the energetics. For simplicity, we neglect the effect of vortices.”

As demonstrated in Yan *et al.*, *Natl. Sci. Rev.* nwag084 (2026), when the temperature satisfies $T > T_{c0}$, with $T_{c0} = T_c - 2T_0$, the vortex core size exceeds the interlayer spacing D_0 . Here, T_{c0} represents the mean-field transition temperature of a decoupled single-layer, T_c is the bulk superconducting transition temperature of the coupled layered system, and $T_0 \equiv (T_c - T_{c0})/2$ parameterizes the interlayer Josephson coupling. In this regime, adopting the uniform magnetic field approximation and neglecting the Josephson vortex lattice are reasonable. For $T < T_{c0}$, the Josephson vortex lattice becomes relevant and modifies the order parameter of the orbital-FFLO state, as discussed in the reference [Yan *et al.*, *Natl. Sci. Rev.*

nwag084 (2026)]. According to Table 1 of the main text, most of the phase diagram shown in Fig. 3 lies within the window of $T > T_{c0}$. Therefore, vortices can be neglected in the calculations for phase diagrams of Fig. 3.

3. Regarding the results shown in Fig. 3, what is the phase region above orb-FFLO region (SC-2) but below B_{c2} ? Why does the B_{c2} seem to increase for thicker sample, which is counterintuitive?

[Our response] In our experiments, we do not observe any further phase transition above the first-order transition line and below $B_{c2,\parallel}(T)$. Therefore, we attribute the whole region to SC-2.

The seemingly larger absolute value of $B_{c2,\parallel}$ in sample S5 (30 nm thick) than S2 (20 nm thick) stems from the increase in the superconducting transition temperature for thicker samples. In Fig. R1 below, we compare the data points normalized by the Pauli limit ($B_p = 1.84T_c$). Within the experimentally measured range, both samples show comparable normalized critical field values. However, linear extrapolations of data

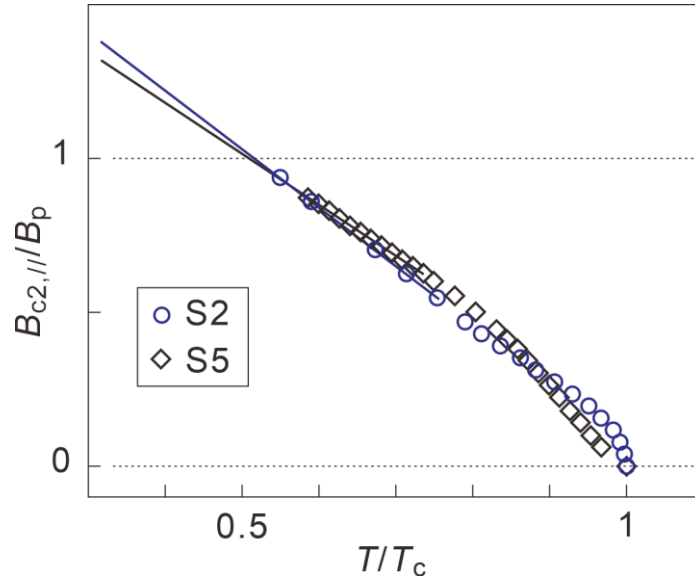


Fig. R1 Normalized in-plane upper critical magnetic field as a function of normalized temperature for samples S2 and S5.

points at low temperatures (straight lines) indicate that sample S2 hosts a slightly larger enhancement.

4. “Due to the increasing energy cost in the uniform Ising superconducting state, a thicker sample therefore tends to transition to the orb-FFLO state at a lower field.” It is unclear to me why thicker sample requires lower field to realize orb-FFLO, and

the change of onset field is so dramatic from 20nm to 30nm thick sample in Figure3. As long as interlayer coupling is weak, I would not expect a significant difference between bilayer and multilayers. Can the authors explain their claim more clearly?

[Our response] We thank the Referee for this comment. For multi-layer Ising superconductors, the layer index enters into the Lawrence-Doniach model as

$$F = \sum_l \int d^2\mathbf{r} \left\{ \frac{\hbar^2}{2M_{\parallel}} \left| \left[\nabla_{\parallel} - i \frac{2\pi}{\Phi_0} B D_0 \left(l - \frac{1}{2}(N+1) \right) \right] \Psi_l(\mathbf{r}) \right|^2 + \alpha |\Psi_l(\mathbf{r})|^2 + \frac{\beta}{2} |\Psi_l(\mathbf{r})|^4 - J [\Psi_l^*(\mathbf{r}) \Psi_{l+1}(\mathbf{r}) e^{-i\chi_{l,l+1}} + c.c.] \right\}, \quad (1)$$

where we have already substituted the expression for $A_{\parallel}$. From Eq. (1), we find that at high magnetic fields, the kinetic energy of a uniform Ising superconducting state increases rapidly with the layer index due to the increase in the magnetic vector potential. By contrast, for orbital-FFLO state, the order parameter has the form: $\Psi_l(x) = f_l(x) e^{iq_l x}$, where $q_l = \frac{2\pi}{\Phi_0} \left[l - \frac{1}{2}(N+1) \right] B D_0$. In this case, the layer-dependent magnetic vector potential across different layers is compensated by the finite-center-of-mass momentum q_l of Cooper pairs. As a result, the kinetic energy cost is reduced, whereas the inter-layer Josephson coupling energy is only slightly increased due to constant momentum difference between adjacent layers. Therefore, the free energy of the orbital-FFLO state is lower than that of the uniform state. Moreover, as the number of layers increases, the compensation becomes more effective. Consequently, the condition for the first-order phase transition, namely, the equality of the free energy of the uniform state and the orbital-FFLO state, is satisfied at a lower magnetic field.

The dependence of the upper critical field on the number of layers [see Supplementary Materials of Yan *et al.*, *Natl. Sci. Rev.* nwag084 (2026)] indicates that, despite weak interlayer Josephson coupling, a multilayer system cannot be easily regarded as a stack of isolated bilayers. The layer number is therefore a key parameter controlling the shift of the first-order phase transition line and leads to the dramatic change of onset field from 20nm to 30nm thick sample.

In the texts before the cited sentence, we describe the different evolution of energy with sample thickness for the Ising superconductor and the orb-FFLO state. To make it more clearly, we have revised the corresponding text. The texts now read as (We highlight the revised text in red):

“The kinetic energy for the uniform Ising superconductor increases with the number of layers under a finite in-plane magnetic field, due to the presence of the magnetic vector potential. In the orb-FFLO state, however, the finite momentum can cancel out the magnetic vector potential such that the kinetic energy maintains a relatively low value. As a consequence of the contrasting thickness dependences of energy described above,

a thicker sample tends to transition to the orb-FFLO state at a lower field."

5. "Our theoretical fitting indicates that the 30 nm thick NbSe₂ hosts such a modulation in the *a*–*b* plane with a period of about 1.6 μ m at an in-plane magnetic field around 1 T, inviting future spatial imaging studies under much less demanding conditions." In the theoretical calculation, the authors assumed FFLO pairing in each layer so that there are even gap modulation within each layer? By the way, in the theoretical part, the authors put the momentum of Cooper pairs in the top half number of layers to be positive *q*, while bottom half number of layers to be negative *q*. But this configuration setting looks different from the one considered in previous Justin Ye's Nature paper, where the Cooper pair momentum is opposite in between two nearest layers.

[Our response] The reviewer is correct that in the orbital-FFLO state the gap exhibits a spatial modulation within each layer. This follows directly from the free energy functional given by Eq. (6) in the Methods:

$$f_o = \frac{1}{2\pi} \int_0^{2\pi} \left\{ \left(\frac{B}{B_{0J}} \right)^2 \left[\frac{d}{d\bar{x}} |f_l(\bar{x})| \right]^2 + \left(\frac{T-T_c}{T_0} + 2 \right) |f_l(\bar{x})|^2 + \frac{\beta}{2J} |f_l(\bar{x})|^4 - 2f_l(\bar{x})f_{l+1}(\bar{x})\cos(\bar{x}) \right\} d\bar{x}.$$

where the gap function $f_l(\bar{x})$ depends on the in-plane coordinate $\bar{x}$ and adjacent layers are coupled through a Josephson coupling term $-2f_l(\bar{x})f_{l+1}(\bar{x})\cos(\bar{x})$. As a result, $f_l(\bar{x})$ is generally non-uniform in $\bar{x}$.

Numerically, we discretize the coordinate $\bar{x}$ over one spatial period (taken as 2π in our dimensionless units) and minimize the free energy density with respect to $f_l(\bar{x})$. The optimized solution yields the spatial profile of the gap $f_l(\bar{x})$ in each layer, as shown in Fig. R2. We find that $f_l(\bar{x})$ varies periodically, confirming the intralayer gap modulation. In addition, the amplitude of the gap is larger in the inner layers and becomes progressively suppressed toward the outer layers of a multilayer Ising

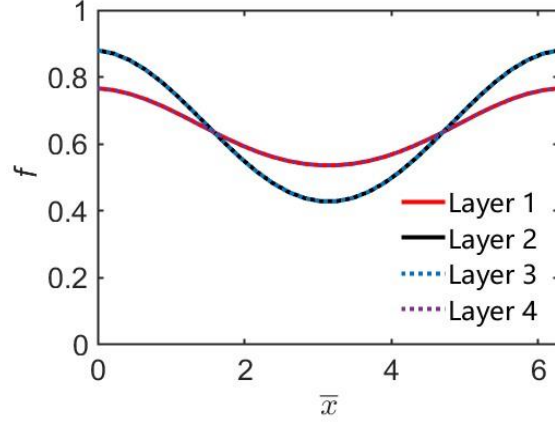


Fig. R2 Spatial modulation of the superconducting gap in different layers of a four-layer Ising superconductor in the orbital FFLO state.

superconductor.

The assignment of q to each layer is indeed different from that in Ye's Nature paper. We have compared the situation that Ye et al. proposed with our situation and found that our situation is energetically more favorable. In our proposed orbital-FFLO state, the difference of the pair momenta between adjacent layers is a constant. We have added a schematic drawing in Fig. 4b. This arrangement allows the phase gradients associated with the in-plane magnetic vector potential to be compensated across different layers, thereby reducing the kinetic energy cost and stabilizing the orbital-FFLO state.

Our configuration is distinct from the patterns discussed in previous works, such as an alternating pattern $(\dots, +q, -q, +q, -q, \dots)$ [P. H. Wan *et al.*, *Nature* **619**, 46 (2023)] or a uniform finite-momentum pattern $(\dots, +q, +q, +q, +q, \dots)$ [N. F. Q. Yuan et al., *Phys. Rev. Res.* **5**, 043112 (2023)]. The calculations presented in the Supplementary Materials of Yan *et al.*, *Natl. Sci. Rev.* nwag084 (2026) demonstrate that, within the superconducting phase and under strong in-plane magnetic fields, the configuration with a constant interlayer momentum difference is energetically more favorable.

Reviewer #2 (Remarks to the Author):

The manuscript entitled "Spectroscopic evidence for a first-order transition to a possible orbital Fulde-Ferrell-Larkin-Ovchinnikov state" by Cao et al. reports tunneling spectroscopy measurements that reveal a first-order phase transition associated with the orbital FFLO state. There are few experimental reports on this topic, and if the observed behavior is intrinsic, it provides strong support for the existence of the orbital FFLO state. Data are nicely shown and the results will be of great interest not only to the people in 2D materials community but also to those in the superconductivity community. I therefore recommend publication in Nature Communications. Below are several minor comments that should be addressed before publication.

[Our response] We would like to thank the reviewer for recommending our work for publication.

1. In Fig. 4, D is defined as the sample thickness, while in line 331, D is named as the interlayer spacing, which is very confusing. In addition, as for $N = D/\xi_c$ in line 398, if D corresponds to the sample thickness, this imply that NbSe₂ layers within the ξ_c are regarded as a single layer in the Lawrence–Doniach model. Is this correct? The situation of the orbital FFLO is not sufficiently clear and a schematic illustration would be helpful for readers.

[Our response] We have replaced D in line 331 and other related places by D_0 to avoid the confusion. The symbol D in $N = D/\xi_c$ is indeed the sample thickness. The reviewer is correct that we assume that several atomic layers within ξ_c constitute a single layer in the Lawrence-Doniach model.

We have added a schematic illustration as Fig. 4b in the revised manuscript to draw the contrast between the Ising superconductor and the orbital FFLO state.

2. Is there any physical reason why the superconducting gap becomes larger in the orbital FFLO phase? In addition, if the tunnel junction size were made to be smaller than the domain size of FFLO phase, would the observed step-like behavior disappear?

[Our response] Theoretically, we compare the total energy for the system in the uniform Ising superconducting state and that for the system in the orbital FFLO state. The phase transition occurs because the orbital FFLO phase hosts a lower energy than the uniform Ising superconducting state at $B_{\parallel} > B_0$. In the Ising superconducting state, the superconducting gap gets continuously suppressed by the in-plane magnetic field. This is the main reason why the Ising superconducting state becomes energetically less favorable than the orbital FFLO state.

In multi-layer Ising superconductors, the layer index enters the Lawrence-Doniach model as

$$F = \sum_l \int d^2\mathbf{r} \left\{ \frac{\hbar^2}{2M_{\parallel}} \left| \left[\nabla_{\parallel} - i \frac{2\pi}{\Phi_0} B D_0 \left(l - \frac{1}{2}(N+1) \right) \right] \Psi_l(\mathbf{r}) \right|^2 + \alpha |\Psi_l(\mathbf{r})|^2 + \frac{\beta}{2} |\Psi_l(\mathbf{r})|^4 - J [\Psi_l^*(\mathbf{r}) \Psi_{l+1}(\mathbf{r}) e^{-i\chi_{l,l+1}} + c.c.] \right\}, \quad (1)$$

where we have substituted the expression for $\mathbf{A}_{\parallel}$ ($\mathbf{A}_{\parallel} = (Bz, 0, 0)$). In the uniform state, the gradient of order parameter vanishes, so the kinetic term is dominated by the gauge contribution. The term $\left| \left[\nabla_{\parallel} - i \frac{2\pi}{\Phi_0} B D_0 \left(l - \frac{1}{2}(N+1) \right) \right] \Psi_l(\mathbf{r}) \right|^2$ becomes increasingly costly for layers with a larger index l . Consequently, to minimize the free energy, the order parameter modulus f_l (i.e., the gap magnitude) is strongly suppressed, especially in the outer layers. In contrast, in the orbital-FFLO state, the order parameter develops layer-dependent phase gradients (finite-momentum) which compensates the magnetic vector potential across difference layers. This compensation substantially reduces the orbital kinetic energy, leaving mainly the residual spatial variation of gap magnitude. As a result, the optimized free energy minimum supports a larger gap magnitude of the orbital-FFLO state than that of the uniform state.

Here below, we calculate the magnetic-field-dependent gap size for the outermost layer. This is experimentally relevant because the tunneling spectroscopy primarily probes the outermost layers. We define the effective gap size as the mean square root of the gap in the orbital-FFLO state, i.e., $\Delta_{\text{eff}} = \sqrt{\langle |\Delta(\bar{x})|^2 \rangle}$ (averaged over one modulation period). The result for a 20 nm-thick sample at a fixed temperature of $T/T_c = 0.6$ is shown in Fig. R3 below. We find that a pronounced jump occurs at the first-order phase transition. In addition, we expect that the sudden jump in the tunneling spectroscopy would only occur once if a single domain is probed.

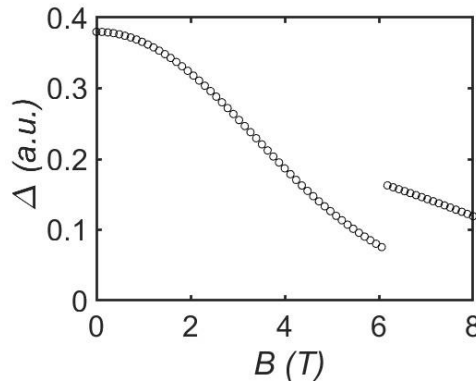


Fig. R3 Calculated superconducting gap as a function of in-plane magnetic field for a 20 nm-thick sample at $T/T_c = 0.6$.

3. Naturally, we expect (B^*, T^*) to coincide with (B_3, T_3) . Is there any physical reason why they differ in the present results?

[Our response] We beg to disagree on the statement that (B^*, T^*) is expected to coincide with (B_3, T_3) . The former point is defined as the deviation point between the experimentally obtained trend of $B_{c2,\parallel}(T)$ and the Ginzburg-Landau fitting. It serves only as an approximate indicator of the phase transition. We experimentally found that the real tri-critical point occurs at slightly higher magnetic field and lower temperature. This is also an important piece of information that can only be gained through tunneling spectroscopy.

4. In the Methods section, authors mentioned that h-BN is etched using CF₄/O₂. Does this process cause oxidization or degradation of the sample? Could sample degradation or resulting inhomogeneity be an alternative explanation for the observed behavior?

[Our response] The etching process only affects the contact area of NbSe₂ while the central area of NbSe₂ for both resistance characterization and tunneling spectroscopy is well protected and unaffected. As demonstrated previously in ref. 7 (*Nature* **619**, 46 (2023)), the up-turn in $B_{c2,\parallel}(T)$ only occurs in samples with high quality. The reproduction of the same up-turn in our sample (sample S2) with a comparable thickness clearly demonstrates that our samples host similarly high quality as those studied previously without using the etching process. Furthermore, we demonstrate in supplementary note 4 that the observed sudden change in dI/dV sensitively depends on the disorder effect: the sudden change in the tunneling spectroscopy gets quickly smeared once the sample quality—reflected by the residual resistivity ratio (RRR)—becomes compromised.

5. There are few typos:

Line 201: “dependenc” → “dependence”

Line 336: “superconcutor” → “superconductor”

[Our response] We have corrected these typos.

Reviewer #3 (Remarks to the Author):

This manuscript reports a systematic transport and spectroscopic study of NbSe₂ flakes with thickness in the 10-30 nm range, aiming to probe the thermodynamic signature of the transition from a uniform Ising superconducting state to the proposed orbital FFLO (orb-FFLO) state induced by an in-plane magnetic field. Using resistance and tunnel spectroscopy measurements, the authors first identify the phase space for the orb-FFLO by confirming the upturn in the field-temperature dependence reported in the literature. Using tunnel spectroscopy based on NbSe₂/WS₂/graphite heterostructures, they observe clear hysteretic changes in the conductance at both zero bias and at the bias corresponding to the coherence peak, consistent with a first-order transition. This behavior is shown to be extremely sensitive to field orientation, appearing only within less than one degree of the in-plane direction. The authors further show that similar behavior can be observed in the closely related NbS₂, but is absent in FeSe, arguing against this being a generic feature of multiband superconductors. On the theory side, they show that the orb-FFLO can be favored in relatively thicker samples over the Ising superconducting state with a uniform order parameter. Moreover, the phase space in the field-temperature phase diagram expands as the sample thickness increases. The calculated phase diagram is in quantitative agreement with the experimental results.

The study of unconventional superconductivity such as the FFLO phase is of central importance in condensed matter physics, and the recently proposed orb-FFLO phase has attracted increasing interest. The observation of thermodynamic evidence for a field-driven transition into this phase is a significant advance, as most previous reports relied on resistance measurements alone and spectroscopic information has been lacking. In this sense, the present work provides more concrete evidence that this phase may indeed exist, and it enables a more reliable determination of the phase diagram because the first-order transition is more clearly revealed. The experiments are well designed and carefully executed, and the manuscript is clearly written, combining theory with careful discussion of alternative scenarios. Overall, I find this work to be of high quality and likely to become an important reference for the field. I have a few issues that I hope the authors can address to further strengthen the manuscript.

[Our response] We appreciate that the reviewer carefully summarized the findings of our work and provided very positive remarks.

Can the authors further clarify their physical understanding of the orb-FFLO? Specifically, the Discussion mentions vortex formation. Do Abrikosov vortices form within the theoretical framework used for the orb-FFLO here? If yes, how do they

interact with, or modify, the orb-FFLO state? If not, why are vortices not expected? Relatedly, how should one understand the effects of disorder on the orb-FFLO?

[Our response] We reason that the vortex lattice stays pinned within the temperature and magnetic field range that we study. The number of vortices increases with the in-plane magnetic field continuously and does not generate any sudden change in the energetics. The motion of vortices is not expected because it would give rise to finite magneto-resistance. In contrast, we obtain zero resistance around B_o . Finite resistance only occurs around B_{c2} , which is far above B_o .

We note that Abrikosov vortices form under a magnetic field perpendicular to layers. In this work, we focus on multilayer Ising superconductors subjected to an in-plane magnetic field, where the vortex structure differs from Abrikosov vortex. As demonstrated in Yan *et al.*, *Natl. Sci. Rev.* nwag084 (2026), when the temperature satisfies $T > T_{c0}$, with $T_{c0} = T_c - 2T_0$, the vortex core size exceeds the interlayer spacing D_0 . Here, T_{c0} represents the mean-field transition temperature of a decoupled single-layer, T_c is the bulk superconducting transition temperature of the coupled layered system, and $T_0 \equiv (T_c - T_{c0})/2$ parameterizes the interlayer Josephson coupling. In this regime, adopting the uniform magnetic field approximation and neglecting the Josephson vortex lattice are reasonable. For $T < T_{c0}$, the Josephson vortex lattice becomes relevant and modifies the order parameter of the orbital-FFLO state, as discussed in the reference [Yan *et al.*, *Natl. Sci. Rev.* nwag084 (2026)]. According to Table 1 of the main text, most of the phase diagram shown in Fig. 3 lies within the validity window $T > T_{c0}$, therefore, vortices can be neglected in the calculations for phase diagrams of Fig. 3.

We have added the following descriptions in the discussion section:

“We also exclude the depinning of vortices or the melting of vortex lattice⁴⁰ as the mechanism for the observed sudden change, because they would give rise to magneto-resistance. By contrast, the resistance stays zero around B_o in our experiment.”

We have also added the following statement in the theoretical note of the Methods:

“Although vortices can enter our samples, they serve as a background and do not generate any sudden change in the energetics. For simplicity, we neglect the effect of vortices.”

Regarding the disorder effect, we expect that the orb-FFLO state to be less sensitive to disorder than the classic FFLO state because the finite momentum occurs between different layers. Still, we experimentally observe that the first-order transition gets smeared as the disorder gets stronger. It indicates that the orb-FFLO state also favors clean superconductivity.

The authors propose that phase transitions occurring in multiple domains are responsible for the hysteresis observed in the differential conductance as a function of magnetic field. If this is the case, should one also expect hysteresis in resistance versus field measurements? If not, please clarify why the domain scenario would produce a pronounced hysteresis in tunneling conductance but not in transport.

[Our response] We would like to point out that we attribute the multiple jumps observed in Fig. 2d/e to multiple domains. We do not intend to attribute the observed hysteresis to multiple domains. In addition, the resistance in the relevant regime stays zero because the phase transition occurs between two superconducting states.

In the Methods, some important experimental details appear to be missing, which are essential for reproducibility by other groups. The authors should explain why WS₂ was chosen as the tunneling barrier. Given possible interfacial charge transfer between WS₂ and NbSe₂, could unusual phenomena arise from the specific properties of this interface, which complicate the interpretation? What thickness of WS₂ was used to optimize the quality of the tunnel spectroscopy data? The device schematic in Figure 1 indicates a trilayer WS₂. Was this tested to be the optimal thickness? Would hexagonal BN be a better choice?

[Our response] The reviewer is correct that a trilayer WS₂ was experimentally found to be the optimal thickness for the tunneling experiment. We found that a bilayer was too thin to be a reliable tunnel barrier and four layers of WS₂ gave rise to very high tunnel resistance. We have added the following sentence in the Methods:

“We experimentally found that a trilayer of WS₂ was the optimal thickness for the tunnel barrier, in comparison to a bilayer or a quadlayer.”

We note that WS₂ is a semiconductor and has been employed as a tunnel barrier in previous experiments. We quote from Bai, et al., *ACS Nano* 16, 7880 (2022) their experimental finding that: *WS₂ can be used as a high-quality, layered tunnel barrier material and that its thickness can be effectively controlled at atomically thin scale.*

Hexagonal BN can serve as a tunnel barrier too but the yield of suitably thin h-BN is much lower from our experience.

The reviewer has raised an interesting scenario about the charge transfer. Experimentally we found that the tunneling spectroscopy yields superconducting gaps of NbSe₂ that are consistent with other studies using the scanning tunneling microscope or a planar junction consisting of MoS₂ or WSe₂ as the tunnel barrier. Therefore, charge transfer is unlikely to account for the sudden phase transition.

Also in this section, two different techniques for differential conductance measurements are introduced, but detailed description is provided only for the current-bias case. Since most samples were measured using the voltage-bias method, the details of that method should be included as well. It is also stated that a four-terminal configuration was used. How exactly were the four terminals wired and used in the two types of measurement? A wiring schematic would be helpful for interested readers.

[Our response] We have added further descriptions on the voltage-biased measurement. We illustrate the wiring for the four-terminal configuration of the current-biased mode in Fig. 1b. The voltage-biased mode is two-terminal and has been added to Supplementary Fig. 2c.

For convenience, we show the revised texts below:

“Tunneling conductance was measured under either a current bias mode (sample S2), as illustrated in Fig. 1b, or a voltage bias mode (Sample S1, S3, S4 and S5), as illustrated in Supplementary Fig. 2. In both modes, the signal applied to the graphite layer consists of the DC bias together with a small AC modulation. In the current bias mode, the AC current was chosen to be 0.5/2.5 nA (typically at a frequency of 3.333 Hz) in measuring the tunneling spectra (Fig. 1e,f) or magnetic field dependence of ZBTC (Fig. 2). The resultant AC voltage across the junction, measured in a four-terminal configuration (as illustrated in Fig. 1b), was demodulated by using a pre-amplifier and a lock-in amplifier. The DC component of the four-terminal voltage was registered by the DC voltmeter. In the voltage bias mode, we employed an AC modulation of 0.1 mV (13.333 Hz) in the measurement of dI/dV as a function of V . The amplitude was increased to 0.5 mV or 1 mV for better signal to noise ratio when we measured $dI/dV(V = 0)$ as a function of $B_{||}$. The resultant AC current through the junction was measured either by using a current pre-amplifier, with its output to the lock-in amplifier, or by measuring the AC voltage across a small resistor connected in series.”

In Table 1, the extracted spin-orbit coupling energy scale for sample S2 is much larger than that for the other samples. A possible explanation should be provided.

[Our response] We explain in the corresponding theoretical note of the Methods that: *“The smaller Δ_{so} of sample S3 than that of sample S2, despite their nearly the same thickness, reflects the fact that sample S3 hosts stronger disorder, which substantially renormalizes the bare spin-orbital coupling strength.”*

Supplementary Figure 5 shows data for sample S4 measured at mK temperatures. The caption states that the color shading indicates the orb-FFLO and the uniform

Ising superconducting state (Ising-SC), but it is unclear how these phases map onto panel c. In panel e, the field-induced change in differential conductance across the first-order transition is less pronounced than that observed at higher temperatures, for example at 1.6 K in Figure 1 for sample S2. Why does the signature of the first-order transition weaken at such low temperature, where thermal broadening is reduced?

[Our response] We would like to thank the reviewer for carefully checking our manuscript and pointing out this inconsistency. We have corrected the wrong statement in the corresponding figure caption. The color-shades only indicate the superconducting state (SC) and the gray shade indicates the normal state (NS).

The reviewer is correct to point out that the magnitude of the field-induced change of sample S4 in Supplementary Fig. 5e seems weaker than that for sample S2. This weakening primarily stems from the stronger disorder effect in sample S4.

Reviewer #1:

The authors have done a great job addressing my comments and improving their manuscript. I now strongly recommend the publication of this version in Nature Communications.

Reviewer #2:

The authors have properly addressed the reviewer's comments and questions. The revisions have significantly improved the clarity of the manuscript. Therefore, I recommend this paper for publication in Nature Communications.

Reviewer #3:

The authors have addressed all my questions. I recommend the publication of this manuscript in Nature Communications.

[Our response] We would like to thank all three reviewers for recommending our work for publication.