Peer Review File

Manuscript Title: Cascade of correlated electron states in a kagome superconductor CsV3Sb5

Editorial Notes:

Redactions – Third Party Material

Parts of this Peer Review File have been redacted as indicated to remove third-party material.

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referee #1 (Remarks to the Author):

Materials with Kagome lattice have attracted much attention recently, as the Kagome lattice is a natural arena for various electronic correlations, such as magnetism, geometric frustrations, nontrivial band topology, and now, superconductivity. A favored consequence of these intensive competing interactions could be the observed "cascade of correlated electron states" claimed by Zhao H. et al., The discovery of XV3Sb5 (X=K, Cs, Rb) certainly generates lots of research interests. There are already four STM reports on this family [1-4]. Although all of them detect the 2x2 CDW order, the proposed exotic phenomena in many cases are absent in others' reports. My major concern is that the 1D stripe order and the rotational symmetry breaking states are likely surface states with trivial origin (e.g. dangling bond, structure distortion, charging or polar effect….). Often, by cleaving a sample, one breaks the chemical bond between different layers. This process may create an unstable surface and induce structural distortions/charge carrier doping near and surface, and therefore drives reconstruction of the electronic states.

The following facts have deepened my doubts:

A significant feature of its surface origination is the STM tip-induced creation/rotation of the unidirectional charge order domain boundary in Ref. [1,2]. Figure S9 e-h show additional non-periodic stripe modulations vary with bias voltages, indicating inhomogeneity or instability. Unlike the 2x2 CDW order, there is a lack of evidence of the 1D stripe order (4a0 1Q-CO) from other transport/bulk spectroscopy measurements.

Stripe wave vectors q2 and q2' fit to the bulk Fermi surface in the inset of Figure 4a. The Fermi surface is also confirmed by ARPES measurements. If q2 (and/or q2') is generated by elastic scattering between multiple parallel stripes of the bulk bands, will the noticeably disperse in Figure 4c match bulk bands? In addition, Figure 4g shows q2 and 1Q-CO rotate in the same way across the domain boundary, indicating the symmetry breaking in Figures 4b-e relates to the modulation of 1Q-CO. As 1Q-CO stripe already breaks rotational symmetry, I do not find why a novel explanation for the 1D nature of q2 is essential.

Is there any dispersion of the q2' vector? How does it compare with q2?

Moreover, figure 2c shows two concentric circles of QPI pattern which resembles Rashba type surface states, as well as Fig. 2d. Again, call for a better understanding of the surface properties in a conventional way.

With these facts in mind, I am not yet convinced that the 1D stripe order and the rotation symmetry breaking are robust bulk states with novel nature.

Then, why does the surface origination matter here? One of the main claims in the manuscript is the "bulk" band topology and symmetry breaking effect relate to the bulk superconductivity, which is "similar to the observed electronic states in cuprate high-temperature superconductors" and indicates "intrinsic topological superconductivity and Majorana modes". All these novel proposals are based on a bulk origination (e.g. "strong energy-dependent orbital renormalization") of thenew symmetry-breaking electronic states.

As no reliable evidence to support the authors' major claims, I find the current version of the manuscript is not suitable for Nature yet.

Reference:

1. Zhao H. et al., Cascade of correlated electron states in a kagome superconductor CsV3Sb5. arXiv:2103.03118 (this work)
2. Chen H. et al., Roton pair density wave and unconventional strong-coupling superconductivity in a topological kagome metal. arXiv:2103.09188
3. Jiang Y-.X. et al., Discovery of topological charge order in kagome superconductor KV3Sb5. arXiv:2012.15709
4. Liang Z.W. et al., Three-dimensional charge density wave and robust zero-bias conductance peak inside the superconducting vortex core of a kagome superconductor CsV3Sb5. arXiv:2103.04760

Referee #2 (Remarks to the Author):

In this article, the authors present their discovery of multiple charge-density-wave (CDW) orders in CsV3Sb5 upon lowering temperature. At higher temperatures, it was found that there exist a period-2 CDW order with three ordering momenta related by six-fold rotations. Upon lowering temperature to ~4.5K, the authors report an additional period-4 CDW order that is unidirectional. With this additional CDW order, the lattice rotational symmetry is broken, as is detected from other features in the quasiparticle interference.

These results seem valid, and are novel in kagome materials. However I do not think it meets the high criteria of Nature for publication in terms of attracting broad interest. Instead I think it is better suited for a more specific journal. On a technical level, I found that the results presented need to be expanded and clarified in order to be more significant.

1) I am confused about the v-shaped spectral gap at Fermi level. In the text, the authors associate it with the CDW order that already develops at ~90K. However, the figure the authors refer to is with data at 4.5K, a temperature at which the unidirectional CDW already develops. Can the authors distinguish the role of the two CDW orders in reconstructing the Fermi surface? Unfortunately I do not see any discussion on the Fermi surface reconstruction due to the charge order.

2) Below 4.5K the lattice rotational symmetry is broken. Other than the features in QPI with momentum q2, are there any other spectral signatures of rotational symmetry breaking? One would expect the peak intensities at the three wave vectors corresponding to the high-temperature CDW order to become different. Additionally, anisotropy should be present in the SC state as well. If these features are absent, a discussion or an tentative explanation is still warranted.

In conclusion, unfortunately I cannot recommend the publication of this paper in Nature.

Referee #3 (Remarks to the Author):

Review of Zhao et al.,

Zhao et al., has performed spectroscopic imaging scanning tunneling microscopy (SI-STM) measurement on a recently discovered topological kagome metal, CsV3Sb5 (Tc~2.5K) as a function of temperature to study electronic structure of this compound. Authors reported different classes of charge orderings in this compound; tri-directional (Q3Q-CO) with 2a0 period and unidirectional (Q1Q-CO) charge orderings with 4a0 period encoded in the topography. These features are also seen in the electronic structures. While Q3Q-CO CDW is observed at elevated temperature and the authors argued that this is a CDW that occurs at T=90K, Q1Q-CO CDW appears around 60K and the strongly anisotropic scattering is observed by the QPI measurement at 4.5K. The authors suggest that the unidirectional Q1Q-CO charge order is arising from electron-electron correlation and the strong anisotropic scattering can be attributed to the orbital-selective renormalization of the V kagome bands as a result of an emergence of the q=0 nematic order.

Data quality is excellent and I can also tell in the data that the authors overcome a technical difficulty in implementing QPI in a large enough field of view (FOV) in this compound, as it seems difficult to obtain a stable "clean" surface since Cs migrates over the FOV. A QPI signature encoded in the topography is one of the most beautiful patterns I have ever seen in the correlated materials. It could be an iconic QPI pattern in a textbook. Detections of the multiple charge orderings and the anisotropic QPI are extremely interesting, and these observations are highly important in understanding an intertwined physics, in which multiple orders are present coupling to each other. The present manuscript possesses originalities, multiple new discoveries and important physics in a timely manner, and thus I recommend a publication to Nature. However, the authors need to address questions and comments below prior to the publication.

1. The authors stated in the manuscript that the Tc of the CsV3Sb5 is about 2.5K, but how is it measured and defined? What's a superconducting volume?

2. In Fig. 1d and S1, the authors presented a surface of the CsV3Sb5 and I can see that there are many Cs atoms on Sb surface. On the other hand, the authors presented data in a fairly big field of view over 100nm without migrated Cs atoms on the Sb surface and succeeded in taking spectroscopic maps. In order to get a good q-space resolution, ~50x50nm2 clean FOV is usually required and it is surprising that the authors secured such large FOV on this sample. How is it obtained? Is there any particular procedure? The authors stated in the method that the sample was cold-cleaved. But what's the exact temperature and how is it cleaved?

3. In Fig. 2c and 4bde, the authors showed two-fold symmetrized Fourier transform of dI/dV(r,V) maps. In general, in order to symmetrize a FT map, all the Bragg peaks must appear exactly at symmetric points of the pixel coordinate. Usually, there is a scanner piezo drift, and a scan direction is not exactly parallel to the crystal axis, so that the Bragg peaks don't appear at the symmetric pixel locations. Thus some type of a distortion correction needs to be performed prior to symmetrize the map. I wonder if the authors applied the distortion correction to the data, and if so, the authors should explain what was exactly performed in the analysis step by step.

4. In Fig2d, the authors used dI/dV(r,V)/I(r,V)/V to perform angular average and constructed the image shown in Fig2d. Why did the authors normalize the dI/dV(r,V)? Such a normalization is typically used to mitigate a so-called "setup effect", and in the case of cupartes Z=dI/dV(r,+V)/dI(r,-V)/dV is often used to study intrinsic electronic modulations (e.g., T. Hanaguri et al., Nature Physics 3, 866 (2007)). Is there a setup effect in raw dI/dV? The authors need to consistently present either dI/dV(r,V) or dI/dV(r,V)/I(r,V)/V throughout the manuscript. Otherwise, it should be explained.

5. An emergence of the CDW implies that a band is reconstructed, and momentum eigenstates where an original band and a translated band are intersect, are gapped out in general. In Fig 2b

and in the manuscript, the authors stated that the dip near the zero bias seen in the averaged dI/dV spectrum is most likely a gap for Q3Q-CO CDW. But, is there any spectral signature associated with the Q1Q-CO CDW? Would the authors be able to see any change in the dI/dV spectra upon emergence of the Q1Q-CO CDW? I propose to discuss these points in the manuscript, if any.

6. In Fig. 3c and 4f, the authors showed the topography on Sb surface, in which energy integrated ripple or QPI is encoded and clearly visible. At centers of the ripples, there are "black holes" acting as a scattering center. But, a size of the hole is much bigger than that of a missing single atom. Is it a cluster of the missing atoms? Is there any explanation/interpretation for them?

7. In Fig. 4f, the authors showed a domain boundary of the unidirectional Q1Q-CO CDW. Is there any "mode" in dI/dV at the domain boundary like the one reported in FeSe0.45Te0.55 (Zhenyu Wang et al., Science 367, 104 (2020))? Or, in other words, is there any topological nature in the electronic structure on this surface the authors studied?

8. The authors claim that the Q1Q-CO CDW and the anisotropic QPI probably occur on different bands. And the authors proposed that the q=0 nematic order can be an origin of the anisotropic QPI and attributed to the orbital selective renormalization of the V band. However, since Q1Q-CO CDW already breaks rotational symmetry of the lattice, the anisotropic QPI can be simply explained by the scattering off potentials generated by the Q1Q-CO CDW or the lattice, which is expected to have a unidirectional structure factor. Thus, a QPI pattern would be unidirectional. It is natural for me to discuss these phenomena as closely related rather than separating to each other. Or, is there any evidence that the Q1Q-CO CDW and the anisotropic scattering emerge at different temperature (or the same temperature)? In Fig. 3e, the authors presented FT linecuts of Fig. 3d at different temperature and the Q1Q-CO CDW seems to appear at T~60K, but is there any QPI measurement around this temperature?

9. The authors presented a QPI result below Tc, as shown in Fig. S7. Is there any change in QPI patterns below and above Tc? When the system enters into the superconducting state, a band is reconstructed in general and the authors should be able to detect a change in the QPI patterns. Is there any signature of the Bogoliubov QPI? Did the authors look at Z-map (=dI/dV(r,+V)/dI(r,-V)/dV) for the data below Tc?

10. The authors also studied electronic structure below Tc at different magnetic fields, as shown in Fig. S7. I wonder if the authors observed any vortices. If not, is there any reason?

11. Similarly to above, is there any change in QPI peak intensities upon applying the magnetic field? Coherence factors determine Bogoliubov quasiparticle amplitudes and are involved in scattering process of QPI, exhibiting enhancement of particular q-vectors although it depends on scatterer species (e.g., scaler or magnetic etc)(See e.g., T. Hanaguri et al., Science 323, 923 (2009)). This is particularly powerful in determining symmetry of the superconducting order parameter. It is also the fact that these arguments may apply to CDW states. So, I wonder if the authors can make a comparison of the QPI intensities as a function of temperatures and discuss coherence factors for CDW above Tc. This comment might be beyond a scope of this manuscript, but scientifically important.

Author Rebuttals to Initial Comments:

We are sincerely thankful to all the Reviewers for their insightful questions and expert advice on how to clarify and strengthen our manuscript. We revised our manuscript accordingly.

- We added the following sections to the Supplementary Information
  - Section 3: Additional discussion on the sample cleaving process and the intrinsic nature of rotation symmetry breaking
  - Section 4: Discussion of spectral gap identification
  - Section 5: Magnetization and transport characterization of bulk single crystals
- We added or revised the following figures:
  - Fig. 2d to show radially averaged Fourier transform linecut in raw dI/dV maps
  - Fig. 4c to add the dispersion of q_2'.
  - Fig. S1b to show the as-cleaved Sb surface topograph with several Cs adatoms
  - Inset in Fig. S2b to show the intra-unit cell location of defects serving as QPI scattering sites
  - Fig. S11c-f to show the QPI scattering origin in more detail.
  - Fig. S13 to show FT amplitude of the three $2a_0$ CDW wave vectors as a function of energy.
  - Fig. S14 to show additional temperature-dependent STM data
  - Fig. S15 to display representative magnetization and magnetotransport measurements
  - Fig. S16 to directly compare the topographs of Sb surface termination in CsV_3Sb_5 and cousin compound KV_3Sb_5
- All major modifications to the main text and the Supplement are left in blue font.

We address the individual questions raised by the Reviewers below.

Referee #1 (Remarks to the Author):

Materials with Kagome lattice have attracted much attention recently, as the Kagome lattice is a natural arena for various electronic correlations, such as magnetism, geometric frustrations, nontrivial band topology, and now, superconductivity. A favored consequence of these intensive competing interactions could be the observed "cascade of correlated electron states" claimed by Zhao H. et al., The discovery of XV3Sb5 (X=K, Cs, Rb) certainly generates lots of research interests. There are already four STM reports on this family [1-4]. Although all of them detect the 2x2 CDW order, the proposed exotic phenomena in many cases are absent in others' reports. My major concern is that the 1D stripe order and the rotational symmetry breaking states are likely surface states with trivial origin (e.g. dangling bond, structure distortion, charging or polar effect….). Often, by cleaving a sample, one breaks the chemical bond between different layers. This process may create an unstable surface and induce structural distortions/charge carrier doping near and surface, and therefore drives reconstruction of the electronic states.

We thank the Reviewer for highlighting the excitement behind the recently discovered family of AV_3Sb_5 kagome superconductors. While our manuscript was the first to report electronic rotation symmetry breaking and $4a_0$ charge ordering in CsV_3Sb_5, the $4a_0$ charge order was also subsequently shown in arXiv preprints by other groups (arXiv: 2103.09188 and 2104.08810), which now involves at least three different sample providers and STM groups. We understand the Reviewer's concern regarding the extent to which our phenomena are representative of the

physics of CsV_3Sb_5 and related to the underlying kagome structure, as opposed to a trivial origin due to the cleaving process, and we sincerely thank him/her for prompting us to elaborate on this more clearly. To address this, we performed new experiments and added a discussion on this in Supplementary Section 3. We highlight major points from that discussion below, which demonstrate that rotation symmetry breaking and $4a_0$ charge order in CsV_3Sb_5 are **not related to trivial origins** (dangling bonds, polar effect, etc.) due to a cleaving process and/or surface reconstruction.

1. For comparison, we investigated the surface of the cousin compound KV_3Sb_5, prepared and cleaved using the equivalent procedure as the CsV_3Sb_5 crystals, and we do not observe $4a_0$ charge ordering there (we now reported this finding in arxiv: 2104.08209, also new Fig. S16). We emphasize that the surface layer is the same in both materials (Sb layer), with the V kagome net directly below. As such, we can rule out that $4a_0$ charge ordering is due to a surface reconstruction because of, for example, dangling bonds or polar effects. If this was the case, we would see the same phenomenon on the Sb surfaceof KV_3Sb_5 as well, but we do not. In analogy to cuprates, the presence of $4a_0$ ordering in CsV_3Sb_5 but not in KV_3Sb_5 may be related to doping changes (concomitant with the threefold change in superconducting T_c). This hypothesis will be explored in future work.

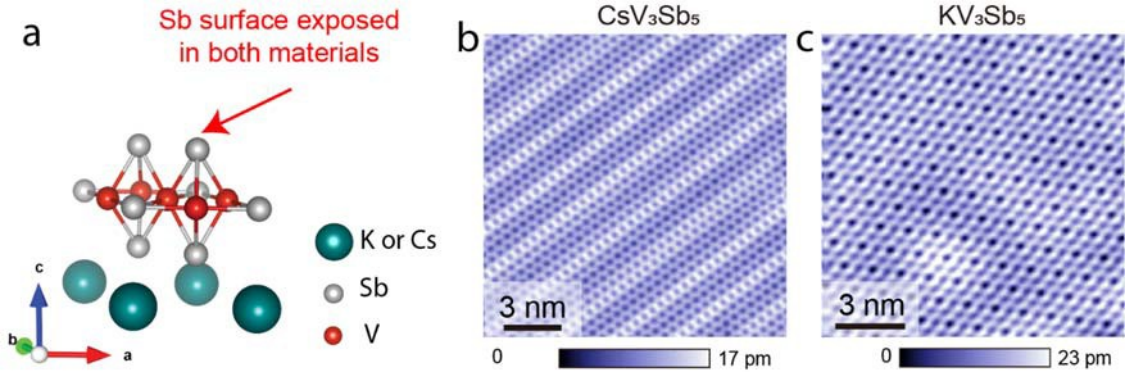


Figure S16. Comparison between CsV_3Sb_5 and KV_3Sb_5. *(a) 3D crystal structure of CsV_3Sb_5 and KV_3Sb_5 showing the same Sb surface termination. (b,c) Typical STM topographs of the same Sb termination in two materials at 4.5 K.*

2. The $4a_0$ charge ordering onsets below ~50 K, and it is not present at higher temperatures (Fig. 3 of the main text, also new Fig. S14). If the $4a_0$ signal was due to a reconstruction associated with the cleavage process, it should in principle be present at all temperatures measured.

3. We performed new magnetotransport measurements, which show that resistivity exhibits a clear two fold-symmetry approaching low temperature as the field is rotated in-plane (Fig. S15b,c). This suggests that rotation symmetry breaking is an intrinsic bulk property.

4. We rule out the structural distortions (strain) for several reasons, as discussed in the last paragraph in the main text on page 4.

5. Guided by theoretical calculations and the morphology of the constant energy contours from ARPES, QPI in Fig. 4 can be traced to scattering from V bulk bands (more details in Fig. S11, Supplementary Section 2). Therefore, the strongly anisotropic QPI signature is

directly related to the rotation symmetry breaking of the electronic bands structure associated with the kagome lattice due to correlation effects.

6. QPI signal from the pocket at Γ primarily composed of Sb orbitals matches the expected Sb bulk bands (Fig. 2, Fig. S5). In principle, given that Sb layer is the topmost surface termination where the symmetry of the crystal is broken, Sb orbitals should be the most prone to a pathological behavior, but we show this is not the case.

We believe that these points sufficiently demonstrate that rotation symmetry breaking is an intrinsic feature of CsV_3Sb_5, intimately related to correlated Vanadium bulk bands, and not an artifact of the cleaving process. Our new experiments on KV_3Sb_5 (arXiv: 2104.08209) show that $2a_0$ x $2a_0$ CDW peaks also exhibit rotation symmetry breaking. This suggests that rotation symmetry breaking may be universal to AV_3Sb_5 superconductors (which will be further discussed in subsequent work focused on KV_3Sb_5), and that the $4a_0$ unidirectional order is a manifestation of the rotational symmetry breaking through an additional positional order.

Since posting our work on the arXiv, we were happy to see preprints from several other experimental groups using *bulk* measurement techniques that support our observations. For example, some of the co-authors of our manuscript collaborated with an ultrafast coherent phonon spectroscopy group that detected an onset of a bulk resonance at 60 K (John Harter group, UCSB). This is nearly identical to the temperature onset of the $4a_0$ charge order we see here, growing in strength approaching low temperature. These results will be published in a separate manuscript (arxiv:2104.10138). Moreover, two-fold resistivity anisotropy, consistent with that shown in our new Fig. S15b, was reported in the same material by two groups (arXiv:2104.00374, arXiv:2104.06909), one of which clearly shows it emerges below 60 K (Hai-Hu Wen group, arXiv:2104.06909). These experiments provide further support that rotation symmetry breaking and unidirectional charge ordering that we have uncovered in our manuscript can be detected as signatures in bulk measurements as well.

The following facts have deepened my doubts:

A significant feature of its surface origination is the STM tip-induced creation/rotation of the unidirectional charge order domain boundary in Ref. [1,2].

We assume that the Reviewer is referring to the unidirectional CDW domain boundary in Fig. 4(f,g). This domain boundary where $4a_0$ charge order rotates by 60 degrees was *not* induced by the tip, but we encountered it by randomly moving the tip around the sample to image different regions. If the Reviewer is referring to Fig. S6 where we are able to switch the direction of the charge order at the domain boundary in 1-2 nanometer regions, we are not sure how that would diminish the significance of our observations or suggest that they are not intrinsic to the system. In our view, this may suggest that the $4a_0$ stripe is a quasi-2D charge order with weak inter-layer coupling, and as such, it may be possible to sometimes tweak the boundaries by the electric field of the tip.

Figure S9 e-h show additional non-periodic stripe modulations vary with bias voltages, indicating inhomogeneity or instability.

We politely disagree with the Reviewer that any modulations varying with bias in STM topographs would indicate some instability. STM topographs contain information on the density of states integrated over all energies from the Fermi energy to the energy corresponding to the STM setup

bias. So as the STM setup bias changes, STM topographs will also appear differently. In fact, this highlights the complexity of this intriguing material. In our system, we have at least two different charge ordering wave vectors, as well as several dispersive quasiparticle interference wave vectors (Fig. 2 and Fig. 4), with different energy scales. The combination of these phenomena will naturally lead to the seemingly bias-dependent inhomogeneous patterns. We emphasize that despite these, the momentum-transfer-space location of charge ordering wave vectors in Fourier transforms of STM data does not change with bias (Fig. 3(g), S3, S4, S9).

Unlike the 2x2 CDW order, there is a lack of evidence of the 1D stripe order (4a0 1Q-CO) from other transport/bulk spectroscopy measurements.

As we briefly mentioned above, there are several pieces of evidence from our STM measurements that we use to demonstrate that rotation symmetry breaking is an intrinsic feature of our system. This now includes transport measurements showing two-fold anisotropy in resistivity measured as a function of angle of in-plane magnetic field (Fig. S15b,c). Moreover, recent resistivity and magneto-transport measurements (arXiv:2104.06909 and arXiv:2104.00374) and optical spectroscopy (arxiv:2104.10138) from other groups all see signatures of unidirectionality and/or onset of bulk phenomena at the same temperature where $4a_0$ charge order emerges in our work (about 50-60 Kelvin). This is strong evidence that the emergence of $4a_0$ charge ordering and pronounced rotation symmetry breaking, first reported in our manuscript, is also reflected in bulk properties.

Stripe wave vectors q2 and q2' fit to the bulk Fermi surface in the inset of Figure 4a. The Fermi surface is also confirmed by ARPES measurements. If q2 (and/or q2') is generated by elastic scattering between multiple parallel stripes of the bulk bands, will the noticeably disperse in Figure 4c match bulk bands?

We thank the Reviewer for this comment, and for allowing us to clarify. We have added a description of the likely scattering processes in Fig. S11. As discussed in more detail in Supplementary Sections 1 and 2, the band structure at low temperature is renormalized as the system enters the CDW state. Therefore, additional refinement of the theoretical model, taking into account both charge ordering states, will be necessary for a complete understanding of the QPI signature and its dispersion related to V bands. Nevertheless, the morphology of q_2 and q_2' (long parallel stripes in q-space) is beautifully consistent with the expected scattering from parallel sheets of the V bands. As such, while we cannot understand all the details of the QPI yet, our data presents strong evidence for the intimate relationship between the QPI in Figure 4 and the electronic band structure related to the V kagome lattice, which is the point we stress in the manuscript.

In addition, Figure 4g shows q2 and 1Q-CO rotate in the same way across the domain boundary, indicating the symmetry breaking in Figures 4b-e relates to the modulation of 1Q-CO. As 1Q-CO stripe already breaks rotational symmetry, I do not find why a novel explanation for the 1D nature of q2 is essential.

The QPI in Fig. 4 ($\mathbf{q_2}$ and $\mathbf{q'_2}$ wave vectors) provides a direct insight into the electronic bands associated with the V kagome lattice (QPI from Sb bands located at the Brillouin zone center is reflected in the wave vector $\mathbf{q_1}$). Given that the system hosts up to three bands crossing the Fermi level, the evaluation of the renormalization of each band is highly desirable. Our measurements provide an access to kagome V bands (expected from theory to be tied to exotic phenomena in kagome systems) and the bands of the Sb "spacer" layer independently. We find that the

renormalization of the V bands at the Fermi level is remarkably pronounced (Fig. 4), while that of the Sb band (**q_1** wave vector in Fig. 2) is almost negligible. As we discuss in the related question of Reviewer #3 (question 8), unidirectionality of the QPI signature is not just a trivial consequence of 1Q-CO, but may have distinct k-space origins as it emerges at different temperature.

Is there any dispersion of the q2' vector? How does it compare with q2?

The dispersion of q_2' follows the same evolution as q_2. We now added this panel to Fig. 4c (also in revised Fig. S11).

Moreover, figure 2c shows two concentric circles of QPI pattern which resembles Rashba type surface states, as well as Fig. 2d. Again, call for a better understanding of the surface properties in a conventional way.

There is actually no indication of Rashba splitting from ARPES measurements at that same energy range (i.e. Ortiz et al, PRL (2020)), and as we show in Fig. 2, the QPI dispersion is reasonably consistent with both theory and ARPES. The second QPI vector (q_1') also emerges far below the Fermi level, so although its understanding is certainly interesting, it should not affect the interpretation of the phenomena observed around Fermi energy.

We further note that Rashba type splitting of a circular constant energy contour would in principle lead to either: (A) 3 concentric circles if all scattering is allowed regardless of the spin, or (B) a single circle if taking into account spin-selective scattering. This has been nicely presented in for example recent work by Peter Wahl group (see Fig. R1 below).

[Redacted]

Fig. R1. *Data and schematic of Rashba splitting on $PdCoO_2$ by Peter Wahl group (Science Advances 7, eabd7361 (2021)). (Left panel, top half) QPI data, and (right) schematic of the Rashba splitting and scattering vectors. With spin-selection, only one QPI vector is seen (red arrow). Without spin-selection another two vectors (dashed pink lines) would have been seen.*

As such, a more natural explanation for the second concentric QPI circle (q_1') is due to different constant energy contour shapes in the k_z-dispersion. This has been shown in the QPI of Fe(Se,S) (Hanguri et al, Science Advances 4, eaar6419 (2018)), where the signal from both k_z=0 and k_z=0.5 has been observed. We explained this in the caption of Fig. 2 by stating:

"*While we cannot conclusively identify **q'_1**, we hypothesize that it may be related to the same band as **q_1**, and that due to a larger **k_z**-dispersion at lower energies, the STM picks out dispersions related to two different, possibly extreme values of **k_z**."*

With these facts in mind, I am not yet convinced that the 1D stripe order and the rotation symmetry breaking are robust bulk states with novel nature.

We are again thankful to the Reviewer for the questions and comments. We believe that our answers to his/her individual questions raised above sufficiently demonstrate the robustness of our results.

Then, why does the surface origination matter here?

In addition to our reply above in regards to Reviewer's question of the surface origin of rotation symmetry breaking and how we demonstrate that it is an intrinsic feature, we also point to the following. As a surface probe, STM is sensitive to the information from the topmost few layers. The surface termination of CsV_3Sb_5 is either a Cs layer prone to a surface reconstruction, or the Sb layer (Fig. 1). The reconstruction of the Cs layer may influence the tunneling signal, and provide information that may not be intrinsic to the bulk of the sample itself. Moreover, imaging through the Cs layer would provide another "spacer" layer, in addition to the Sb layer, necessary to tunnel through to reach the V kagome plane beneath. As such, the relevant signal from the kagome plane may be subdued. For these reasons, we focus on imaging the complete Sb layer in this work.

One of the main claims in the manuscript is the "bulk" band topology and symmetry breaking effect relate to the bulk superconductivity, which is "similar to the observed electronic states in cuprate high-temperature superconductors" and indicates "intrinsic topological superconductivity and Majorana modes". All these novel proposals are based on a bulk origination (e.g. "strong energy-dependent orbital renormalization") of the new symmetry-breaking electronic states.

We point again to our QPI measurements, which can directly access both Sb (Fig. 2) and V (Fig. 4) bulk bands. Our new analysis shows hints of rotation symmetry breaking even in the $2a_0$ CDW state (Fig. S13), which is now a well-established bulk order detected by many probes. As noted previously, emerging experimental evidence has detected signatures of bulk phenomena with an onset temperature of 60 K, nearly identical to the onset of $4a_0$ charge order here, including our transport measurements in Fig. S15.

We also want to clarify that we did not mean to imply that our work "indicates" intrinsic topological superconductivity and Majorana modes, as the Reviewer comments. We apologize if this was not clear enough. We simply mention some of the outstanding questions future experiments should focus on. We revised the sentence to add the appropriate references, which now reads:

"*Future experiments should address the competition of different phases by a more detailed temperature-, energy- and doping-dependent measurements, while also searching for evidence of intrinsic topological superconductivity and Majorana modes expected to arise in this family of materials due to their intrinsic non-trivial band topology* [29]. "

As no reliable evidence to support the authors' major claims, I find the current version of the manuscript is not suitable for Nature yet.

With the addition of new data, analysis and a more detailed discussion, we believe that we now provide even stronger evidence to demonstrate the robustness of our findings. We establish that charge ordering and QPI related to V kagome bands all display C_6->C_2 rotation symmetry breaking along the same lattice direction, providing a unified picture of rotation symmetry breaking in this novel superconductor, below and above superconducting T_c. These results have attracted significant amount of interest in the community in recent weeks, with several bulk measurements beginning to support our observations. We hope that the revised version of the manuscript is now suitable for publication in Nature.

Referee #2 (Remarks to the Author):

In this article, the authors present their discovery of multiple charge-density-wave (CDW) orders in CsV3Sb5 upon lowering temperature. At higher temperatures, it was found that there exist a period-2 CDW order with three ordering momenta related by six-fold rotations. Upon lowering temperature to ~4.5K, the authors report an additional period-4 CDW order that is unidirectional. With this additional CDW order, the lattice rotational symmetry is broken, as is detected from other features in the quasiparticle interference.

These results seem valid, and are novel in kagome materials. However I do not think it meets the high criteria of Nature for publication in terms of attracting broad interest. Instead I think it is better suited for a more specific journal. On a technical level, I found that the results presented need to be expanded and clarified in order to be more significant.

We thank the Reviewer for praising the validity of our results and the novelty of observations in kagome materials. We address the Reviewer's comment regarding "attracting broader interest" in the following paragraphs.

Transition-metal based kagome lattice materials provide a versatile and exciting platform for exploring geometrically frustrated, correlated, and topological quantum states of matter. The field has recently leapt forward with the discovery of superconductivity on a quasi-2D kagome lattice in vanadium-based kagome metals AV_3Sb_5. Since the submission of our work to the arXiv in early March, there has already been 30+ new papers on AV_3Sb_5 systems posted on the arXiv, with the vast majority of them citing our manuscript. These materials have gained significantly traction of the community, which continues to expand. Many research groups from the U.S., Asia, and Europe are currently studying AV_3Sb_5 kagome superconductors, using a wide range of techniques including sample growth, ARPES, STM, Josephson junctions, transport, NMR, optics, neutron and x-ray scattering, as well as theoretical studies.

We also emphasize that the observations reported in our paper are quite surprising. While theory predicted numerous possibilities for translation and rotation symmetry breaking of the kagome lattice electronic structure, experimental realization of these phases has been challenging. Our discovery of the unidirectional $4a_0$ charge order is a huge surprise, new even to the theoretical community. Our report that not one, but multiple charge order states exist in CsV_3Sb_5, with different wave vectors and geometries, and that these states spontaneously break the rotation symmetry of the lattice, has already sparked the effort in the community to understand the nature of these phases theoretically, as well as by other experimental tools. As we more strongly demonstrate in the revised manuscript, temperature-dependence of the anisotropic QPI reveals that its onset is at a different temperature compared to the two charge ordering wave vectors, which suggests the existence of q=0 nematic state possibly indicative of orbital ordering. Interplay of electronic phenomena observed here shows intriguing similarities to high-temperature superconductors, in a cleaner (undoped) system that may be easier to understand, and as such, will likely be of interest to a broad scientific community beyond those focused on kagome materials.

For these reasons, we strongly believe our manuscript satisfies the high criteria of broad interest for publication in Nature.

1) I am confused about the v-shaped spectral gap at Fermi level. In the text, the authors associate it with the CDW order that already develops at ~90K. However, the figure the authors refer to is

with data at 4.5K, a temperature at which the unidirectional CDW already develops. Can the authors distinguish the role of the two CDW orders in reconstructing the Fermi surface? Unfortunately I do not see any discussion on the Fermi surface reconstruction due to the charge order.

We thank the Reviewer for this comment. Our statement in the original manuscript was indeed a bit confusing, and we apologize for that. The Reviewer's question regarding the role of different CDWs in gapping the Fermi surface is also very insightful. With additional data we have acquired, we can shed a bit more light on the issue now.

First, we can provide an upper bound on the magnitude of the spectral gap, if any, on the electron pocket at Γ to be ~1-2 meV, based on our thermal resolution and the fact that the QPI signal is clearly present near Fermi energy (Fig. S5). Therefore, all charge ordered states are gapping out the bands near the Brillouin zone edge, which are primarily comprised of V kagome orbitals. It is possible that the Sb band is not gapped at all, and that the CDW is orbital selective.

Second, we have acquired some temperature-dependent spectroscopic measurements to determine the evolution of the spectral gap through the temperature of $4a_0$ charge ordering onset around 50 K (Fig. S14, also on the right). We can see that the broad V-shape (shoulders at ± 20 mV, which become much more prominent at 4.5 K) persists to 50 K. This may suggest that the smaller gap-like feature observed at 4.5 K is related to $4a_0$ charge order.

We discuss this in the concluding paragraphs of the main text:

"The formation of this $2a_0$-CO order leads to the larger spectral gap in d*I*/d*V* spectra with shoulders around ± 20 meV (inset in Fig. 2b, Fig. S14(c)), which we identify based on its temperature dependence (Supplementary Section 4) and recent ARPES measurements [38]. This gap opening at the Fermi level should be primarily associated with V bands, given that our high-resolution QPI measurements at low-temperature put a bound on the gap of the Sb pocket at Γ to be 1-2 meV (Fig. S5)."

To benefit the reader and explain the phenomena to the best of our current understanding, we also added a discussion to Supplementary Section 3.

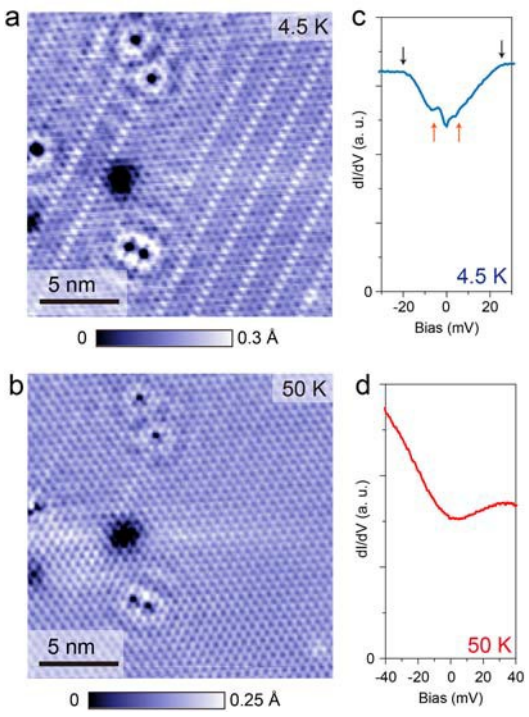


Figure S14. *(a,b) STM topographs of an identical area of the sample at (a) 4.5 K, and (b) 50 K, and (c,d) corresponding spatially-averaged dI/dV spectra. As it can be seen from (b), the $4a_0$ charge ordering is nearly completely absent at the elevated temperature. The low-temperature dI/dV spectra show two shoulders at +/- 20 mV (black arrows) and two closer to Fermi energy around +/- 5-10 mV (orange arrows). dI/dV spectra at higher temperature (just before entering the $4a_0$ charge ordering state) only show the broad shoulders at higher energy.*

Lastly, we note that while these measurements provide some constraints on the momentum-space origin of the gap, and general energy scales that may be related to different charge orders, we are unable to conclusively demonstrate the origin of the gaps solely from STM measurements.

A complicating factor also lies in the possible gap anisotropy, where different parts of the Fermi surface are gapped by different magnitudes even on the same pockets. In fact, this seems to be the physical picture emerging from recent ARPES measurements (i.e. arXiv:2104.08042). High-resolution temperature-dependent ARPES will be an ideal tool in future experiments to convincingly map out the momentum- and band-dependent spectral gaps, and compare to our findings.

2) Below 4.5K the lattice rotational symmetry is broken.

While lattice rotation symmetry is certainly broken below 4.5K, we want to clarify here that this symmetry breaking onsets at a much higher temperature of at least 50-60 Kelvin (Fig. 3e) where the $4a_0$ unidirectional charge order sets in.

Other than the features in QPI with momentum q2, are there any other spectral signatures of rotational symmetry breaking? One would expect the peak intensities at the three wave vectors corresponding to the high-temperature CDW order to become different.

We sincerely thank the Reviewer for this question. Consistent with Reviewer's expectation, Fourier transform amplitudes of the $2a_0$ x $2a_0$ CDW peaks also exhibit rotation symmetry breaking (Fig. S13, below). Specifically, we can see that the Fourier transform amplitude as a function of energy (bias) is nearly identical for two directions (two shades of green squares in Fig. S13b), but the third direction is noticeably different (orange squares in Fig. S13b). We added this analysis to the Supplementary Figure S13.

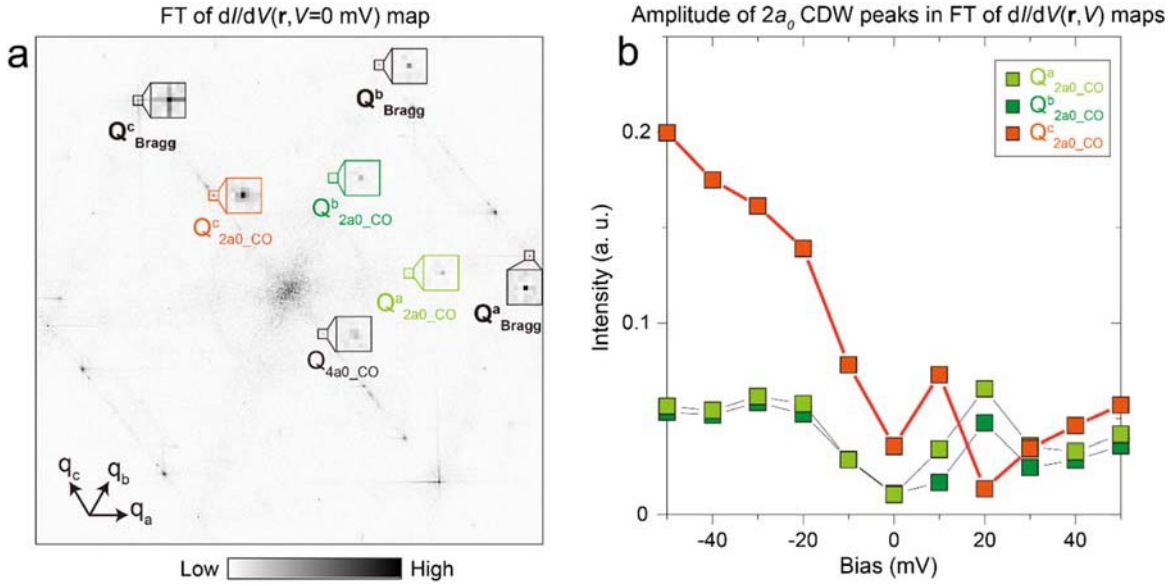


Figure S13. Energy dependence of the Fourier transform amplitude of the $2a_0$ by $2a_0$ CDW at 4.5 K. *(a) Fourier transform (FT) of differential conductance dI/dV(r,V=0 mV) map acquired over the sample region from Figure 2. (b) The amplitude of different CDW peaks in the FTs of dI/dV(r,V) maps as a function of STM bias V. While the dispersions of $Q^a_{2a0\_CO}$ and $Q^b_{2a0\_CO}$ are nearly identical, the dispersion of $Q^c_{2a0\_CO}$ (which is along the direction of the $4a_0$ charge ordering peak Q_{4a0}) is markedly different.*

Additionally, anisotropy should be present in the SC state as well. If these features are absent, a discussion or an tentative explanation is still warranted.

We indeed observe anisotropy in the QPI signal in the superconducting state as well (Fig. S7). We comment on this in the main text in the last paragraph*: "Lastly, we note that sub-Kelvin SI-STM measurements reveal that symmetry-broken states persist well below the superconducting T_c (Fig. S7) …"*

Based on suggestions from Reviewer #3, we will aim to perform more challenging magnetic field and temperature-dependent QPI measurements in the superconducting state in the future, to shed light on the nature of superconducting pairing. However, we believe this should not delay the current manuscript, which contains several other exciting results on a newly discovered material.

In conclusion, unfortunately I cannot recommend the publication of this paper in Nature.

We thank the Reviewer for the pertinent questions, which allowed us to further strengthen our manuscript. We emphasize again that AV_3Sb_5 kagome superconductors have recently emerged as one of the most intriguing new materials. Our work presented the first report of C_6->C_2 rotation symmetry breaking in AV_3Sb_5, reflected in multiple channels, with a fascinating range of different energy- and temperature- scales. Our results have already attracted a large interest, not only within the quickly increasing AV_3Sb_5 community, but also the quantum materials community in general due to striking similarities to phenomena observed in correlated electron systems and unconventional superconductors. The material studied here provides a rare, if not unique, playground for exploring multiple charge ordering states with different wave vectors and geometries coexisting with superconductivity, electronic nematicity and a partial band-selective gapping of different portions of the Fermi surface. As such, we strongly believe it meets the high bar for publication in Nature.

Referee #3 (Remarks to the Author):

Zhao et al., has performed spectroscopic imaging scanning tunneling microscopy (SI-STM) measurement on a recently discovered topological kagome metal, CsV3Sb5 (Tc~2.5K) as a function of temperature to study electronic structure of this compound. Authors reported different classes of charge orderings in this compound; tri-directional (Q3Q-CO) with 2a0 period and unidirectional (Q1Q-CO) charge orderings with 4a0 period encoded in the topography. These features are also seen in the electronic structures. While Q3Q-CO CDW is observed at elevated temperature and the authors argued that this is a CDW that occurs at T=90K, Q1Q-CO CDW appears around 60K and the strongly anisotropic scattering is observed by the QPI measurement at 4.5K. The authors suggest that the unidirectional Q1Q-CO charge order is arising from electron-electron correlation and the strong anisotropic scattering can be attributed to the orbital-selective renormalization of the V kagome bands as a result of an emergence of the q=0 nematic order.

Data quality is excellent and I can also tell in the data that the authors overcome a technical difficulty in implementing QPI in a large enough field of view (FOV) in this compound, as it seems difficult to obtain a stable "clean" surface since Cs migrates over the FOV. A QPI signature encoded in the topography is one of the most beautiful patterns I have ever seen in the correlated materials. It could be an iconic QPI pattern in a textbook. Detections of the multiple charge orderings and the anisotropic QPI are extremely interesting, and these observations are highly important in understanding an intertwined physics, in which multiple orders are present coupling to each other. The present manuscript possesses originalities, multiple new discoveries and

important physics in a timely manner, and thus I recommend a publication to Nature. However, the authors need to address questions and comments below prior to the publication.

We sincerely thank the Reviewer for praising the high quality of our data, recognizing the novelty and timeliness of our work, and recommending the publication in Nature. We address individual questions and comments below.

1. The authors stated in the manuscript that the Tc of the CsV3Sb5 is about 2.5K, but how is it measured and defined? What's a superconducting volume?

We measured zero-field cooled magnetization, which shows a nearly 100% volume fraction. These measurements are consistent with earlier work reporting the synthesis and characterization of the same crystals (Ortiz et al, PRL 125, 247002 (2020)). The superconducting T_c was defined as the approximate onset of Meissner state. We added bulk characterization of our samples in Fig. S15a, and we refer to it from the Methods section in the main text.

2. In Fig. 1d and S1, the authors presented a surface of the CsV3Sb5 and I can see that there are many Cs atoms on Sb surface. On the other hand, the authors presented data in a fairly big field of view over 100nm without migrated Cs atoms on the Sb surface and succeeded in taking spectroscopic maps. In order to get a good q-space resolution, ~50x50nm2 clean FOV is usually required and it is surprising that the authors secured such large FOV on this sample. How is it obtained? Is there any particular procedure? The authors stated in the method that the sample was cold-cleaved. But what's the exact temperature and how is it cleaved?

We thank the Reviewer for this remark. The cleaving process was not sufficiently explained in the original version of the manuscript. We added a detailed description to Supplementary Section 3, and we refer to it from the Methods section. The gist of the process is the following.

To minimize the migration of Cs atoms, we try to cleave CsV_3Sb_5 single crystals at as low temperature as possible. This includes inserting an un-cleaved crystal with a short 1-2 mm cleaving rod attached to it directly into the STM, where it is thermalized for 30 minutes to reach 4.5 K (the tip is retracted so that the cleave rod does not crash the tip). Then, we use the transfer rod to bring the sample back to the UHV preparation chamber, cleave the sample while it is still on the transfer rod, and re-insert the cleaved sample back in STM (this process lasts for about one minute). This results in temperature that is lower than the typical ones that we get using a liquid nitrogen cleaver (explained further in Supplementary Section 3).

We also note that as-cleaved Sb surface will typically have a handful of Cs atoms sprinkled around (one example shown in Fig. S1b). To create large areas for SI-STM measurements free of Cs adatoms, we use the STM tip to sweep the few extra Cs adatoms towards the side of the field-of-view by using low junction resistance. We note that rotation symmetry breaking $4a_0$ charge ordering is also observed on the as-cleaved surface *before* the sweeping process (Fig. S1b shows the as-cleaved surface with a handful of Cs adatoms before they are moved), but we can only obtain 10-20 nm square region of the sample.

3. In Fig. 2c and 4bde, the authors showed two-fold symmetrized Fourier transform of dI/dV(r,V) maps. In general, in order to symmetrize a FT map, all the Bragg peaks must appear exactly at symmetric points of the pixel coordinate. Usually, there is a scanner piezo drift, and a scan direction is not exactly parallel to the crystal axis, so that the Bragg peaks don't appear at the symmetric pixel locations. Thus some type of a distortion correction needs to be performed prior

to symmetrize the map. I wonder if the authors applied the distortion correction to the data, and if so, the authors should explain what was exactly performed in the analysis step by step.

We use the Lawler-Fujita drift-correction algorithm to align the atomic Bragg peaks in STM topographs to be exactly equal in magnitude and 60 degrees apart. The algorithm produces a set of "drift-fields" that specifies how much each pixel in raw data is offset from a perfect hexagonal lattice. We then apply the same drift-fields to simultaneously acquired STM dI/dV maps. After this process, the FT of drift-corrected dI/dV maps is two-fold symmetrized (mirror symmetrized) around the direction of the $4a_0$ charge ordering wave vector direction.

We added this clarification to the caption of Fig. S5, where we show the data before and after symmetrization process. We also added a brief description in the Methods section (highlighted in blue font in both).

4. In Fig2d, the authors used dI/dV(r,V)/I(r,V)/V to perform angular average and constructed the image shown in Fig2d. Why did the authors normalize the dI/dV(r,V)? Such a normalization is typically used to mitigate a so-called "setup effect", and in the case of cupartes Z=dI/dV(r,+V)/dI(r,-V)/dV is often used to study intrinsic electronic modulations (e.g., T. Hanaguri et al., Nature Physics 3, 866 (2007)). Is there a setup effect in raw dI/dV? The authors need to consistently present either dI/dV(r,V) or dI/dV(r,V)/I(r,V)/V throughout the manuscript. Otherwise, it should be explained.

We thank the Reviewer for this comment. Indeed, different normalization conditions can in principle be used, and this should be explained. In the case of cuprates, Z-map normalization, which divides positive energy maps by the corresponding negative energy maps, was particularly useful for particle-hole symmetric-phenomena that are out-of-phase across the Fermi level. As such, this normalization allowed the suppression of checkerboard signal (same phase and wave vector at both positive and negative bias) from the Bogoilubov QPI, which is in turn effectively enhanced. This normalization is unlikely to be useful in our case as we are looking at QPI that is not symmetric with respect to zero energy.

An alternative option occasionally used is the L-map (L(r,V)= dI/dV(r,V)/(I(r,V)/V)) applied in for example Hanaguri et al, *Science Advances* 4, eaar6419 (2018) and Kostin et al, *Nature Materials* 17, 869 (2018). We employed this in the old version of Fig. 2d. However, as the overalldispersions in raw dI/dV maps and the L-maps look comparable, this may be unnecessary. For consistency, we are happy to follow the Reviewer's advice. We now show raw dI/dV maps throughout the text, and we substituted Fig. 2(d) with the equivalent radially averaged dispersionin FTs of dI/dV maps.

5. An emergence of the CDW implies that a band is reconstructed, and momentum eigenstates where an original band and a translated band are intersect, are gapped out in general. In Fig 2b and in the manuscript, the authors stated that the dip near the zero bias seen in the averaged dI/dV spectrum is most likely a gap for Q3Q-CO CDW. But, is there any spectral signature associated with the Q1Q-CO CDW? Would the authors be able to see any change in the dI/dV spectra upon emergence of the Q1Q-CO CDW? I propose to discuss these points in the manuscript, if any.

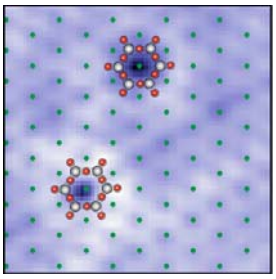
This is a very interesting question. To shed light on the origin of the spectral gap features near the Fermi level, we imaged and compared the same area of the sample at 4.5 K and 50 K (newly added Fig. S14). STM topographs show that $4a_0$ charge ordering, present at 4.5 K, is nearly

completely absent at 50 K (Fig. 14(a,b)), which allows us to compare spectral features before and after the onset of $4a_0$ charge ordering. The low-temperature d*I*/d*V* spectra show two sets of features: (1) shoulders at ± 20 mV and (2) gap-like features closer to Fermi energy around ± 5 to 10 mV (Fig. S14c). In contrast, d*I*/d*V* spectra at 50 K only show the broad shoulders at higher energy (Fig. S14d). This may suggest that smaller gap-like features at 4.5 K (orange arrows in Fig. S14c) are related to the $4a_0$ charge ordering gap. The larger spectral gap at ±20 mV would then correspond to the $2a_0$ CDW. This interpretation is in good agreement with the recent ARPES measurements (Wang et al, arXiv: 2104.05556 (2021); Nakayama et al, arXiv: 2104.08042 (2021)), where a gap opening, starting around 15-20 mV below Fermi level, was detected below the onset temperature of the $2a_0$ CDW phase. The V-shape of the spectral weight suppression at the Fermi level observed in our work (Fig. S14c,d) is also consistent with the anisotropic nature of the gap observed in the aforementioned ARPES experiments.

We now add the new data to Fig. S14, elaborate on the discussion in Supplementary Section 4, and refer to both of these from the main text when we introduce the spectral gap observation.

6. In Fig. 3c and 4f, the authors showed the topography on Sb surface, in which energy integrated ripple or QPI is encoded and clearly visible. At centers of the ripples, there are “black holes” acting as a scattering center. But, a size of the hole is much bigger than that of a missing single atom. Is it a cluster of the missing atoms? Is there any explanation/interpretation for them?

The Reviewer is perfectly correct that the dark defects in STM topographs, around which the QPI ripples are formed, are a bit bigger than a single atom. Their apparent size varies from one to a few lattice constants in diameter depending on the imaging bias. We do not think they are clusters of missing atoms based on their circular shape (we would naively expect a cluster to have an irregular shape). We also note that the dark signature in the topograph does not necessarily imply a missing atom. For example, on metallic surfaces, CO adsorbate molecules are often seen as similar dark “pits” (i.e. Grothe et al, *PRL* **111**, 246804 (2013)). With that being said, we do not think our dark defects are adatoms, as we have not been able to move them around with our STM tip.



Inset from Fig. S2. *Green spheres are the underlying Cs atoms, which are centered around each V-Sb hexagon. Dark defects are centered at the Cs site.*

Prompted by the Reviewer’s comment, we looked into this a bit further. The main insight into their origin from our data comes from their intra-unit-cell position (added as an inset in Fig. S2, also on the right), which shows the defects are centered on the Cs site. This may mean they are related to Cs defects below the kagome plane, possibly vacancies at the Cs site. This is just a hypothesis however, and we note that in the caption of Fig. S2. Future theoretical work could shed light on exact origin by modeling spectral and spatial signature of various defects in this family of materials.

7. In Fig. 4f, the authors showed a domain boundary of the unidirectional Q1Q-CO CDW. Is there any “mode” in dI/dV at the domain boundary like the one reported in FeSe0.45Te0.55 (Zhenyu Wang et al., Science 367, 104 (2020))? Or, in other words, is there any topological nature in the electronic structure on this surface the authors studied?

We have not observed any modes at the boundary. Given the theoretically expected non-trivial electronic topology with topological surface states (Ortiz et al, PRL 125, 247002 (2020)) in analogy to Fe(Te,Se), CsV_3Sb_5 may provide an alternative platform to investigate 1D modes. At this point however, we are not yet sure what other ingredients would need to be met for the

emergence of similar 1D modes in CsV_3Sb_5, but this is certainly an interesting direction to explore in the future, both theoretically and experimentally.

8. The authors claim that the Q1Q-CO CDW and the anisotropic QPI probably occur on different bands. And the authors proposed that the q=0 nematic order can be an origin of the anisotropic QPI and attributed to the orbital selective renormalization of the V band. However, since Q1Q-CO CDW already breaks rotational symmetry of the lattice, the anisotropic QPI can be simply explained by the scattering off potentials generated by the Q1Q-CO CDW or the lattice, which is expected to have a unidirectional structure factor. Thus, a QPI pattern would be unidirectional. It is natural for me to discuss these phenomena as closely related rather than separating to each other. Or, is there any evidence that the Q1Q-CO CDW and the anisotropic scattering emerge at different temperature (or the same temperature)? In Fig. 3e, the authors presented FT linecuts of Fig. 3d at different temperature and the Q1Q-CO CDW seems to appear at T~60K, but is there any QPI measurement around this temperature?

We very much appreciate these insightful questions. To explain the reasons behind our statement, we point to the following.

1) The Reviewer is perfectly correct that the two phenomena have the same rotational symmetry, and that a unidirectional modulation can serve as a unidirectional scattering potential, similar to for example step edges. However, a unidirectional structure factor should in principle predominantly enhance scattering along a single direction, and effectively suppress scattering along other directions, *across all energies.* What we see in QPI is a peculiar reversal of intensity with energy (Fig. 4e): the dominant direction is strong near zero energy, but then it disappears at above +14 meV, just as the QPI along the other two lattice directions emerges.

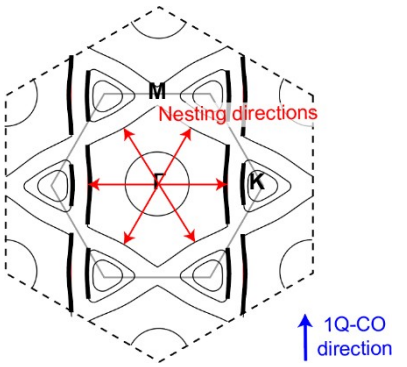


Fig. R2. *Schematic of the Fermi surface with the three nesting directions (red arrows) and the direction of 1Q charge order that is oriented 30 or 90 degrees away from the nesting direction.*

2) Parallel sheets that the QPI arises from could naturally favor the formation of a CDW due to nesting. However, if this was the case, $4a_0$ charge ordering wave vector would have been rotated by 30 degrees (Fig. R2 on the right). We wanted to mention this in the discussion by stating: *"… It poses an intriguing puzzle: canonically unidirectional CDWs are associated with a Peierls instability (at twice the Fermi wave vector) of quasi-1D bands; however, the wave vector of the 1Q-CO (along Γ-M) is perpendicular to the nesting vector connecting the quasi-1D V bands (along Γ-K)."*

Previously, we only acquired temperature-dependent topographs, not QPI maps, to compile Fig. 3(e), since topographs can be acquired much faster than dI/dV maps used for QPI imaging. Prompted by the Reviewer's question, we took additional QPI maps at elevated temperature. Interestingly, we find that the QPI signature weakens substantially, and that it is completely gone at about 30 K, well below the $4a_0$ charge order onset of about 50 K (Fig. S14). This further substantiates the possibility of a true q=0 nematic order, possibly originating from different portions of the band structure compared to the $4a_0$ order, which we hinted at in the previous

version of the text. We added the data to Fig. S14, and made the following modifications to the text:

"In fact, temperature-dependent QPI measurements reveal that the anisotropic QPI vanishes by 30 K, while the $4a_0$ 1Q-CO is still clearly present at that temperature (Fig. S14). This provides an intriguing difference between the two phenomena, despite the same two-fold rotation symmetry."

9. The authors presented a QPI result below Tc, as shown in Fig. S7. Is there any change in QPI patterns below and above Tc? When the system enters into the superconducting state, a band is reconstructed in general and the authors should be able to detect a change in the QPI patterns. Is there any signature of the Bogoliubov QPI? Did the authors look at Z-map (=dI/dV(r,+V)/dI(r,-V)/dV) for the data below Tc?

We will respond to this question along with the related question #11 below.

10. The authors also studied electronic structure below Tc at different magnetic fields, as shown in Fig. S7. I wonder if the authors observed any vortices. If not, is there any reason?

We have not observed vortices, but we have also not extensively looked for them yet. One of the problems is the relatively low H_c of the system, which requires very large areas to detect even a single vortex in the field of view. Based on arXiv:2103.04760, it seems that it is possible to detect one vortex on the Cs surface over a 250 nm square region. We are yet to find a pristine Sb surface of that size for vortex imaging.

11. Similarly to above, is there any change in QPI peak intensities upon applying the magnetic field? Coherence factors determine Bogoliubov quasiparticle amplitudes and are involved in scattering process of QPI, exhibiting enhancement of particular q-vectors although it depends on scatterer species (e.g., scaler or magnetic etc)(See e.g., T. Hanaguri et al., Science 323, 923 (2009)). This is particularly powerful in determining symmetry of the superconducting order parameter. It is also the fact that these arguments may apply to CDW states. So, I wonder if the authors can make a comparison of the QPI intensities as a function of temperatures and discuss coherence factors for CDW above Tc. This comment might be beyond a scope of this manuscript, but scientifically important.

We are thankful to the Reviewer for the expert advice in comments #9 and #11, which outline experiments that we (and I am sure other groups) will pursue in the future. To be confident of the comparison between data below and above T_c, and also in the presence or the absence of magnetic field below T_c, we would need high-resolution density-of-states maps at the two conditions *with the same STM tip*. We have not been able to achieve this yet, but hope to be able to successfully perform these experiments in the coming months. These experiments are not directly related to the main claims of the paper in hand, and as the Reviewer kindly notes, and we agree, they may be beyond the scope of this manuscript.

Reviewer Reports on the First Revision:

Referee #1 (Remarks to the Author):

Given the recent reports as well as the new data from the authors, I am very convinced that "the rotation symmetry breaking is an intrinsic bulk property". However, my major concern is still the bulk origin of the 1D stripe order. My take of all the recent reports is that the rotation symmetry breaking is due to the 2×2 chiral charge order of the bulk, which is a novel phenomenon. And this symmetry breaking effect seems to be a universal feature among the AV3Sb5 family. While the 4a0 superlattice only resides on the surface with different origins. One possible reason is, as the authors suggested in the rebuttal, "In analogy to cuprates, the presence of 4a0 ordering in CsV3Sb5 but not in KV3Sb5 may be related to doping changes". Or "the 4a0 unidirectional order is a manifestation of the rotational symmetry breaking through an additional positional order". Nevertheless, unlike the 2x2 charge order, the 4a0 unidirectional order has not been detected by a bulk X-ray measurement. Mainly, the authors' arguments are based on the different onset temperatures for different orders. This is not strong evidence from my point of view, as different probes possess different sensitivity of the anisotropy. On the other hand, the symmetry breaking effect gets smeared at high temperatures, hampering identification of the onset temperature.

If there is an additional and bulk origin of the 4a0 superlattice in CsV3Sb5, then among the AV3Sb5 family, there will be two intrinsic mechanisms for rotational symmetry breaking. Moreover, the response to my previous question: "In addition, Figure 4g shows q2 and 1Q-CO rotate in the same way across the domain boundary, indicating the symmetry breaking in Figures 4b-e relates to the modulation of 1Q-CO." implies another symmetry breaking effect for q2. Together, we will have at least three different rotational symmetry breaking effects (of bulk origin) in the AV3Sb5 family, which is unlikely to me. Therefore, I personally find the main text is still misleading, which mainly focuses on a surface superlattice. Instead, the 2×2 chiral charge order, most likely, generates the bulk rotational symmetry breaking.

Unfortunately, I cannot recommend the publication of this paper in Nature.

Referee #2 (Remarks to the Author):

In this revised manuscript, the authors improved the quality of their work by acquiring additional data, some addressing my earlier questions regarding the onset of 4a_0 CDW and the anisotropy of the 2a_0 CDW at low temperatures.

In response to the author's reply and revised manuscript, I have several comments.

1) I do not have any doubt that transition-metal based kagome lattice materials are a very important class of materials, potentially hosting a wealth of novel states of matter. However, the class of material alone does not warrant the inherent merit of the discovery. In the example mentioned by the authors, the discovery of charge-density-wave (CDW) order of cuprate high-Tc superconductors, many studies on which published on Nature, was considered significant because of its relation with various experimental features and putative phases of matter in the pseudogap region, which has since lead to the concept of "intertwined order". For the same reason, in my opinion, only when the discovery of CDW's is shown to be relevant in the broader context of the fundamental properties of kagome lattice materials, these results are significant enough to meet the criteria of Nature.

From this perspective, I still am not convinced that this manuscript meets the stringent requirement on novelty and potential impact. This being said, the authors' new results on the relation between various CDW orders does improve the quality of this work.

2) In the new manuscript and in the reply letter, the authors claims that the absence of anisotropic QPI at ~30K and the presence of 4a0 CDW is indicative of a q=0 nematic order. I object to this statement.

Since density-wave orders often break rotational symmetry just as nematic orders do, the term "nematic order" has been reserved to phases that breaks rotational symmetry *but not translational symmetry*. The intimate relation between density-wave order and nematic order has been well studied in the context of iron- and copper-based superconductors. In both cases, "nematic phases" are regions preserving translational symmetry, which can be viewed as a vestigial order from partially melting a unidirectional density-wave states.

In the present context, (a) in the proclaimed "nematic" region at ~30K, translational symmetry remains broken by the 4a CDW. (b) Despite the fact that the QPI anisotropy itself can be explained by a completely unrelated q=0 rotational-symmetry breaking order (which is unlikely, in my opinion), here the onset of this phenomenon does not correspond to *any additional* symmetry breaking.

For these reasons, unless new results clearly show evidence of rotational symmetry breaking *in the absence* of translational symmetry breaking, I don't think it is proper to claim this region possibly displays a q=0 nematic order, and to make any connections to other studies of nematicity, such as Potts pneumaticity in twisted bilayer graphene.

Referee #3 (Remarks to the Author):

Reply to the comment by Zhao et al.,

I would like to thank authors to provide point-by-point answers to my comments. Overall, I think that the authors answered all the points I raised in my comments and it’s all clear now. Accordingly, the manuscript and supplementary information are modified appropriately and are converted into shapes that are suitable for a publication in Nature now. The only comments that I have is a format related issue; the guideline says that no figures are included in the supplementary information. Instead, the authors may have “Extended Data Figures”. Thus, the authors need to rearrange the format of the supplementary information and Extended Data Figures, as well as callouts in the main text.

Author Rebuttals to First Revision:

Referee #1 (Remarks to the Author):

Given the recent reports as well as the new data from the authors, I am very convinced that "the rotation symmetry breaking is an intrinsic bulk property". However, my major concern is still the bulk origin of the 1D stripe order. My take of all the recent reports is that the rotation symmetry breaking is due to the 2×2 chiral charge order of the bulk, which is a novel phenomenon. And this symmetry breaking effect seems to be a universal feature among the AV3Sb5 family. While the 4a0 superlattice only resides on the surface with different origins.

We are happy to learn that the Reviewer now agrees that the rotation symmetry breaking is an intrinsic bulk property of this system.

Before turning to the Reviewer's concern regarding the bulk origin of the $4a_0$ charge order, we first briefly address the Reviewer's conviction that the rotation symmetry breaking in AV_3Sb_5 is due to a 2 x 2 "chiral" charge order.

1. Theoretically, a chiral order is a very exciting idea as it can be tied to time-reversal symmetry breaking via orbital currents. Scientifically, our present work does not focus on or address whether the 2 x 2 CDW in CsV_3Sb_5 breaks time-reversal symmetry. Instead, we focus on the surprising spatial symmetry-breaking phenomena we discovered in CsV_3Sb_5, which we can strongly support and ubiquitously observe in all samples studied.

   Regarding the Reviewer's conviction of charge order chirality, we note that there has indeed been several STM reports claiming the chiral 2 x 2 charge order that breaks time-reversal symmetry on *some* areas of the AV_3Sb_5 samples, primarily driven by the same group of authors (Jiang et al, *Nature Materials* (2021), arXiv:2105.00550, arXiv:2105.04542). They arrive at this conclusion predominantly based on the change in the intensities of the Fourier peaks associated with the CDW upon the reversal of the magnetic field direction. This is clearly an important state, if confirmed by other groups in a scientific process. However, to-date this effect has not been reproduced by other STM groups world-wide that are trying to detect it (ours and two other groups we have communications with). We have been unable to detect any field-induced change in the CDW in our data and analysis, in the vicinity or away from impurities, in 5+ datasets in CsV_3Sb_5 or KV_3Sb_5. We discussed some of the reasons for the discrepant results in our new manuscript (arXiv:2104.08209): the magnetic field dependence may be artificially created by STM tip artifacts. This has to be carefully taken into the account, but it has not been considered in the manuscripts reporting the chirality of the CDW order. Note that this does NOT imply that time-reversal symmetry breaking CDW order does not exist – rather, its existence may not be robustly detectable by STM. We hope that other measurement probes more naturally suited for the detection of time-reversal symmetry breaking will more convincingly demonstrate this in the near future. Nevertheless, we reiterate that our work here explores novel electronic states breaking different *spatial* symmetries beyond the time-reversal symmetry in AV_3Sb_5.

2. A chiral bulk charge order should not break the six-fold rotational symmetry of the system (see for example arXiv: 2103.07097). As such, rotation symmetry breaking and the two-fold electronic structure observed in the form of the $4a_0$ charge stripe order (Fig. 3), QPI measurements (Fig. 4), and resistivity anisotropy (Fig. S15) cannot be explained by a 2 x 2 chiral charge order. As we have noted in our preprint on KV_3Sb_5 (arXiv:2104.08209), and also in the theoretical paper (arXiv:2104.08425), rotation symmetry breaking in the 2 x 2 CDW state may come from the off-phase layer stacking of the 2 x 2 CDW along the *c*-direction,

which naturally breaks the C_6 rotation symmetry. However, this symmetry breaking should occur just below the 2 x 2 CDW transition temperature of ~95 K, the temperature at which the stacking is set. This does not explain the sharp onset of the experimentally detectedresistance anisotropy (arXiv: 2104.06909) near the onset temperature of the $4a_0$ unidirectionalcharge order.

For these reasons, it is difficult to see how the emergence of a C_2-symmetric bulk state would have to be connected to a 2 x 2 chiral charge order, as the Reviewer suggests. Available experimental facts clearly indicate that the rotation symmetry breaking has a different symmetry and a very natural connection to the emergence of the $4a_0$ unidirectional charge order.

Now, we turn to the Reviewer's primary concern about the bulk origin of the $4a_0$ charge stripe order. We are thankful for the Reviewer's elaboration on the issue – we now understand that the Reviewer expected the confirmation of the $4a_0$ charge stripe order from X-ray scattering experiments. However, it is unclear to us why the lack of such a challenging experiment would negatively impact the relevance of this charge order and preclude the publication of the present manuscript. As we elaborate in the remainder of the response:

- The $4a_0$ stripe order is clearly rooted in a bulk phenomenon based on complimentary bulk measurements.
- Given the topological *surface* states expected in these materials and the quasi-2D nature of this family of kagome materials, any co-existing surface or bulk phenomenon should in principle be highly relevant as well.
- The detection of any unidirectional charge stripe ordering via X-ray measurements is incredibly difficult.

We stress that ample experimental evidence from several groups find that the resistivity anisotropy onsets quite sharply around 50-60 K (arXiv:2104.06909; Supplementary Information in DOI: 10.21203/rs.3.rs-355323/v1), which agrees with the onset temperature of the $4a_0$ charge order, and is far below the onset of the 2 x 2 CDW phase. This agreement strongly suggests that there is a bulk rotational symmetry breaking state that emerges below ~50 K, which is either the interlayer coupled $4a_0$ charge order, or a different rotational symmetry breaking state that manifests itself on the surface as the $4a_0$ charge order we discovered. Moreover, coherent phonon spectroscopy (arXiv:2104.10138) has unveiled a phonon resonance that also onsets around the same temperature of the $4a_0$ order (Fig. R1). Consistent with this resonance that strengthens as the temperature is lowered (Fig. R1a), we point out that the amplitude of the $4a_0$ charge

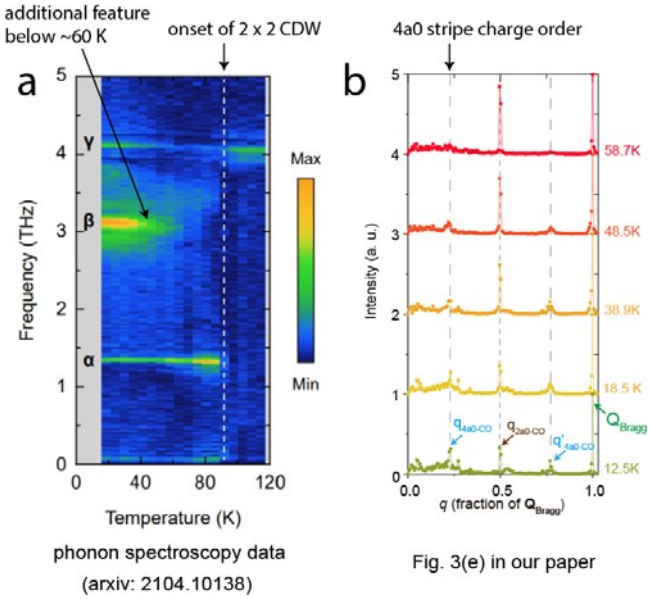


Fig. R1. *(a) Phonon spectroscopy measurements of CsV3Sb5 adapted from arXiv:2104.10138 (Harter group, UCSB), and (b) Fourier transform amplitude profile from our data in Fig. 3(e).*

order in our STM data also follows a temperature dependent increase (Fig. R1b).

Taking these together, we can conclude that there are at least *three* different experimental tools that detect an onset of a new phenomenon at the same temperature of T*~50-60K: STM, resistivity measurements and ultrafast coherent phonon spectroscopy. The Reviewer would surely agree that it is highly unlikely to be coincidental.

To comment on the nature of the $4a_0$ charge stripe phase, we added the following:

"Magnetotransport experiments on CsV_3Sb_5 observed resistivity anisotropy that onsets around 50-60 K[39,40], which agrees with the onset temperature of the $4a_0$ charge order. This agreement strongly suggests that there is a bulk rotational symmetry breaking state that emerges below 50-60 K, which is either the interlayer coupled $4a_0$ charge order, or a different rotational symmetry breaking state that manifests itself on the surface as the $4a_0$ charge order. We note that a new phonon resonance also emerges around the temperature of the $4a_0$ onset[41], thus providing further evidence for the intimate relationship between the $4a_0$ charge order and the bulk of this material."

One possible reason is, as the authors suggested in the rebuttal, "In analogy to cuprates, the presence of 4a0 ordering in CsV3Sb5 but not in KV3Sb5 may be related to doping changes". Or "the 4a0 unidirectional order is a manifestation of the rotational symmetry breaking through an additional positional order".

In the last round of review, we already excluded trivial origins of the $4a_0$ charge order that Reviewer 1 asked us to consider: dangling bonds, polar effect, etc. due to a cleaving process and/or surface reconstruction. As we hypothesized in the previous rebuttal, and now state in the revised manuscript, the observation of the $4a_0$ charge order in CsV_3Sb_5 (and recently RbV_3Sb_5), but not KV_3Sb_5 could be related to band filling (chemical potential difference across different members of this family of kagome superconductors), or small changes in the electronic band structure. It is unclear to us how that would diminish the importance of our results – if anything, it provides a potential tuning knob for the control of this charge ordering state.

To discuss our hypothesis on how the $4a_0$ charge order may be tuned across this family of kagome superconductors, we added the following to the third to last paragraph (top of page 5):

"… chemical potential changes or small band structure variations could possibly explain the presence (Fig. 3) or the absence[36] of the $4a_0$ charge order in different members of the AV_3Sb_5 family."

Nevertheless, unlike the 2x2 charge order, the 4a0 unidirectional order has not been detected by a bulk X-ray measurement.

The presence of quasi-1D correlations cannot be identified in the current high-resolution synchrotron X-ray scattering measurements. This, however, does not rule out the presence of such correlations, and we believe that the present set of X-ray diffraction experiments would be unable to detect these correlations. The reason for this is due to the weak nature of the superlattice that forms below the CDW transition. The 3D superlattice peaks that form in the CDW state appear as Bragg peaks (points in q-space) that are 4 to 5 orders of magnitude weaker than the primary Bragg peaks from the undistorted structure. These are difficult to detect without adequate counting times at a synchrotron source, and these 3D superlattice peaks would quickly melt into the experimental background as their correlation lengths became shorter (and the scattering became more diffuse in q-space). For quasi-1D scattering (one of the more extreme

limits of diffuse scattering), a component of this weak superlattice scattering would necessarily diffuse into planes of intensity distributed throughout q-space. This renders the signal hard to detect in unspecialized experiments and the background must be carefully accounted for at all temperatures. Furthermore, the present reported scattering measurements would necessarily average over all twins that form, which means they will average over at least three possible twin domains in a quasi-1D state (ie. stripes along *a*, stripes along *b* and stripes along (-1,1)). This means that the expected diffuse planes of scatter will additionally further blend into the background as each twin will simply contribute to the overall background in the nominal HK-plane. Future, targeted scattering experiments (possibly in strained crystals to mitigate domain formation) will be necessary to conclusively address the presence of quasi-1D scattering below 60 K in CsV_3Sb_5.

Given that it took 10+ years to clearly detect charge ordering in for example Bi-based cuprates by X-ray measurements after the initial observation by STM, the same high-resolution X-ray experiments will take some time, too.

To comment on the technical challenge of detecting the charge stripe order by X-ray experiments, we added:

"We note that weak quasi-1D correlations are often difficult to detect in traditional survey X-ray measurements due to the diffuse scattering signal falling below the measurement's ability to isolate it from the background. The likely presence of domain boundaries exacerbates this. Targeted scattering experiments, possibly in strained crystals to mitigate domain formation, will be necessary to determine if the $4a_0$ charge stripe order exhibits bulk correlations."

Mainly, the authors' arguments are based on the different onset temperatures for different orders. This is not strong evidence from my point of view, as different probes possess different sensitivity of the anisotropy. On the other hand, the symmetry breaking effect gets smeared at high temperatures, hampering identification of the onset temperature.

We interpret the Reviewer's comment to say that he/she believes that the onset of resistivity anisotropy in magnetoresistance measurements, pinpointed to be around 50-60 K by at least two groups (arXiv:2104.06909; Supplementary Information in DOI: 10.21203/rs.3.rs-355323/v1) and the onset of additional phonon resonance in ultrafast spectroscopy experiments also at 60 K (arXiv:2104.10138) actually occurs at 95 K, and therefore corresponds to the onset of the 2 x 2 CDW order instead of the $4a_0$ order. We stress that we have used a comparison between well-established techniques by reputable groups providing high-resolution experimental data and analysis. It is hard to imagine how a sharp onset in resistivity anisotropy at 50-60 K can be a result of smearing a "true" transition at 95 K that re-emerges 35-45K below that temperature. We therefore disagree with the reviewer's opinion that these bulk measurements indicating a bulk transition at 50-60K can be confused with the 2 x 2 CDW transition at ~95 K.

In summary, what we are trying to convey is that a new phenomenon clearly emerges at a temperature well below the onset of the 2 x 2 CDW transition, detected by multiple different measurement techniques.

If there is an additional and bulk origin of the 4a0 superlattice in CsV3Sb5, then among the AV3Sb5 family, there will be two intrinsic mechanisms for rotational symmetry breaking. Moreover, the response to my previous question: "In addition, Figure 4g shows q2 and 1Q-CO rotate in the same way across the domain boundary, indicating the symmetry breaking in Figures

4b-e relates to the modulation of 1Q-CO." implies another symmetry breaking effect for q2. Together, we will have at least three different rotational symmetry breaking effects (of bulk origin) in the AV3Sb5 family, which is unlikely to me.

We detected three different electronic observables that exhibit the *same* two-fold symmetry of the electronic ground state. It is unclear to us why this would be deemed as too many and thus unlikely by the Reviewer, regardless of their bulk or surface origin. We summarize the physical picture *as demonstrated by our data* as follows:

- A $2a_0$ x $2a_0$ CDW sets in at ~95 K, which breaks the translation symmetry of the lattice.
- The $4a_0$ charge stripe order onsets between 50 and 60 K, which further breaks the rotation symmetry of the lattice.
- Two-fold anisotropy in QPI q_2 vector, directly related to kagome V orbitals, becomes apparent below 30 K, strengthening towards lower temperatures.
- Superconductivity emerges below 2.5 K and coexists with both 2 x 2 and the $4a_0$ charge order, in the ground state that breaks both the translation and rotation symmetries.

We reiterate that the electronic band structure of this material is complex – this is a multi-orbital/multi-band system with multiple van Hove singularities near the Fermi level. Different charge ordering states can simply gap out distinct portions of the Fermi surface; the anisotropy in QPI, which again has the same two-fold symmetry, could be a reflection of the heightened electronic anisotropy approaching low temperatures, or as we note in the text, possibly another phenomenon due to a difference in the onset temperature.

We agree that the phenomenology we have uncovered is rich, but it is unfair to conclude there is something wrong with our work just because there is too many interesting observations. Our data is of the highest quality, repeated multiple times on different CsV_3Sb_5 crystals, and we provide some direct connections to bulk sensitive measurements.

Therefore, I personally find the main text is still misleading, which mainly focuses on a surface superlattice. Instead, the 2×2 chiral charge order, most likely, generates the bulk rotational symmetry breaking.

Unfortunately, I cannot recommend the publication of this paper in Nature.

In summary, we mention again that our present work is unrelated to whether the 2 x 2 CDW in CsV_3Sb_5 state breaks time-reversal symmetry or not, so we did not discuss the potential emergence of the chiral charge order in the present paper. A bulk chiral CDW order would not create a two-fold symmetric state seen in STM and by magnetotransport. Experimental evidence clearly suggests that the $4a_0$ charge order is rooted in an intrinsic bulk phenomenon, and onsets at the same temperature where resistivity anisotropy is detected, along with an onset of a new phonon resonance. Therefore, we strongly disagree with the Reviewer that our focus on charge stripe ordering is misleading. In fact, we present a coherent picture of rotation symmetry breaking in this system resulting in a two-fold electronic structure. Charge density waves and rotation symmetry breaking have been long sought-after in kagome structures, and we provide an experimental realization of these phenomena. With the latest round of changes presented here, we believe that the text now presents a balanced description of the novel physics we uncovered in this exciting new material.

Referee #2 (Remarks to the Author):

In this revised manuscript, the authors improved the quality of their work by acquiring additional data, some addressing my earlier questions regarding the onset of 4a_0 CDW and the anisotropy of the 2a_0 CDW at low temperatures.

In response to the author's reply and revised manuscript, I have several comments.

1) I do not have any doubt that transition-metal based kagome lattice materials are a very important class of materials, potentially hosting a wealth of novel states of matter. However, the class of material alone does not warrant the inherent merit of the discovery. In the example mentioned by the authors, the discovery of charge-density-wave (CDW) order of cuprate high-Tc superconductors, many studies on which published on Nature, was considered significant because of its relation with various experimental features and putative phases of matter in the pseudogap region, which has since lead to the concept of "intertwined order". For the same reason, in my opinion, only when the discovery of CDW's is shown to be relevant in the broader context of the fundamental properties of kagome lattice materials, these results are significant enough to meet the criteria of Nature.

From this perspective, I still am not convinced that this manuscript meets the stringent requirement on novelty and potential impact. This being said, the authors' new results on the relation between various CDW orders does improve the quality of this work.

We are very thankful to the Reviewer for praising the improved quality of our manuscript. We highlight several reasons why our work meets the criteria of relevance, novelty and potential impact mentioned by the Reviewer.

Let us first address the Reviewer's specific benchmark that our discovery should be relevant to the broader context of fundamental properties of kagome materials to meet the bar for publication in Nature. A fundamental property of a single-orbital model on the kagome lattice *at the van Hove filling* under long range Coulomb interaction is the q=0 Pomeranchuk instability towards a rotational symmetry breaking state [i.e. Wang et al, PRB 87, 115135 (2013)]. Here, we have discovered experimental signatures of rotation symmetry breaking on a kagome lattice, albeit with the concomitant unidirectional breaking of the lattice translation symmetry. Intriguingly, subleading divergences of the susceptibility are predicted to occur at all q along the Gamma-M directions emanating from the q=0 Gamma point [i.e. Wang et al, PRB 87, 115135 (2013)]. This may lead to the propensity of the electronic state to also break lattice translation symmetry for realistic band parameters and correlations. It is also conceivable that the translation symmetry breaking observed here via charge ordering wave vectors is related to the off van Hove filling in real materials. The presence of the $4a_0$ charge order in CsV_3Sb_5 and RbV_3Sb_5, but not inKV_3Sb_5, can certainly be consistent with this picture – band structures of the three materials are quite similar, but the chemical potential (and the filling of the band towards/away from the van Hove point) evolves gradually from KV_3Sb_5 on one side to CsV_3Sb_5 on the other. Therefore, our work on CsV_3Sb_5 may provide the first experimental glimpse into additional spontaneous symmetry-breaking electronic states that can emerge on a correlated kagome lattice away from van Hove filling in real materials.

In terms of novelty, the emergence of superconductivity in the presence of both a 2 x 2 charge order and a $4a_0$ charge stripe order is new and nontrivial. Additionally, the co-existence of CDWs and Z_2 topology in the same system (recent ARPES measurements already reveal signatures of

topological surface states in arXiv:2104.12725) is also rare, and possibly unique. As any topological surface state should in principle follow the same symmetry of the co-existing charge ordered states, our work provides a foundation for the explorations of spatial symmetry breaking effects on topological states including potential topological superconductors.

Next, we elaborate on the potential impact. Multi-orbital/multi-band nature of AV_3Sb_5 on a hexagonal lattice in a stoichiometric system with saddle points close to the Fermi level provides new opportunities compared to existing unconventional superconductors. In fact, it is remarkable that we find that the $4a_0$ charge order could be present up to 50-60 K in CsV_3Sb_5 but absent in KV_3Sb_5 down to 4 K despite an extremely similar band structure. As we also noted above, this is an exciting opportunity to explore the mechanism of tuning this state, possibly via filling at or away from the van Hove saddle point. What happens away from the van Hove filling in a kagome system is a fascinating problem, but theoretically, there is no universal prediction of the phase diagram of different instabilities yet. Our results will surely impact the development of theories to explain our novel experimental observations.

We also mention that the $4a_0$ charge order and the rotational symmetry breaking are of general interest as the phenomena of "dimensional reduction", where quasi-1d physics emerges in 2d or 3d frustrated systems. The physics of stripes in cuprates has been extensively discussed in these terms. In our work, the $4a_0$ charge order appears quite one dimensional, and the two-fold symmetric QPI signature in the experiments also has the character of $2k_F$ oscillations of a quasi-1d Fermi surface.

Lastly, as the Reviewer expertly points out in the comment below, it remains to be understood if a vestigial order from partially melting the charge stripes in CsV_3Sb_5 can exist above the $4a_0$ transition point, or in KV_3Sb_5 where the $4a_0$ order is seemingly absent, but signatures of unidirectionality are still there. The electronic structure supporting the $4a_0$ stripes in the superconducting state may also be related to the emergence of a pair density wave in the same material. These are just some of the exciting questions that our work opens up, with concrete experimental and theoretical work to follow, which should significantly impact the direction in this field.

We added some of this discussion in the concluding paragraphs:

> *"A fundamental property of a single-orbital model on the kagome lattice at the van Hove filling under long range Coulomb interaction is the q=0 Pomeranchuk instability towards a rotational symmetry breaking state[17]. Our measurements uncover experimental signatures of rotation symmetry breaking on a kagome lattice, albeit with the concomitant breaking of the lattice translation symmetry. Subleading divergences of the susceptibility predicted to occur at all wave vectors along the Γ-M directions emanating from the Γ point[17] may lead to the propensity of the electronic state to additionally break lattice translation symmetry for realistic band parameters and correlations. It is also conceivable that the translation symmetry breaking via charge ordering is related to the off van Hove filling in real materials. Such chemical potential changes or small band structure variationscould possibly explain the presence (Fig. 3) or the absence[36] of the $4a_0$ charge order in different members of the AV_3Sb_5 family. "*
>
> *"It remains to be understood if a vestigial order may develop from partially melting the $4a_0$ charge stripes."*

"At the same time, the coexistence of multiple charge orders with different wave vectors, geometries and temperature onsets in CsV_3Sb_5 adds to the complexity of the underling physics."

With the more clearly outlined relevance of our results and extended discussion, combined with the undeniable surge of interest in the community in the physics of this new family of materials, we hope that the Reviewer is now more inclined to recommend our work for publication.

2) In the new manuscript and in the reply letter, the authors claims that the absence of anisotropic QPI at ~30K and the presence of 4a0 CDW is indicative of a q=0 nematic order. I object to this statement.

Since density-wave orders often break rotational symmetry just as nematic orders do, the term "nematic order" has been reserved to phases that breaks rotational symmetry *but not translational symmetry*. The intimate relation between density-wave order and nematic order has been well studied in the context of iron- and copper-based superconductors. In both cases, "nematic phases" are regions preserving translational symmetry, which can be viewed as a vestigial order from partially melting a unidirectional density-wave states.

In the present context, (a) in the proclaimed "nematic" region at ~30K, translational symmetry remains broken by the 4a CDW. (b) Despite the fact that the QPI anisotropy itself can be explained by a completely unrelated q=0 rotational-symmetry breaking order (which is unlikely, in my opinion), here the onset of this phenomenon does not correspond to *any additional* symmetry breaking.

For these reasons, unless new results clearly show evidence of rotational symmetry breaking *in the absence* of translational symmetry breaking, I don't think it is proper to claim this region possibly displays a q=0 nematic order, and to make any connections to other studies of nematicity, such as Potts pneumaticity in twisted bilayer graphene.

We are again very thankful to the Reviewer for the insightful comment. The Reviewer is perfectly correct to note the confusing terminology used in the previous version of our manuscript. As the Reviewer agrees, the QPI anisotropy could in principle be explained by a q=0 rotational symmetry breaking order. However, given the translational symmetry breaking by the $4a_0$ charge order, the term 'nematic' would not be appropriate. To correct this, we removed the term 'nematic' from the second to last paragraph and the sentences discussing Potts nematicity.

Referee #3 (Remarks to the Author):

Reply to the comment by Zhao et al.,

I would like to thank authors to provide point-by-point answers to my comments. Overall, I think that the authors answered all the points I raised in my comments and it's all clear now. Accordingly, the manuscript and supplementary information are modified appropriately and are converted into shapes that are suitable for a publication in Nature now. The only comments that I have is a format related issue; the guideline says that no figures are included in the supplementary information. Instead, the authors may have "Extended Data Figures". Thus, the authors need to rearrange the format of the supplementary information and Extended Data Figures, as well as callouts in the main text.

We are sincerely grateful to the Reviewer for the insightful questions in the previous round of the review and the recommendation to publish our manuscript in Nature.

Reviewer Reports on the Second Revision:

Referee #1 (Remarks to the Author):

I truly appreciate the authors' patience. There is no doubt that the AV3Sb5 family provides a unique platform to study the correlated CDW orders as well as band topology/superconductivity with Kagome lattice. Right now, there is an improved balance between proposing the "hypothesis" and demonstrating the experimental facts. My previous comments and suggestions are mainly aimed to attract enough attention from the authors when associating the "4a0 order" and "the bulk rotational symmetry-breaking phenomena". This is crucial given the fact that the authors' new experiment shows KV3Sb5 possesses rotational symmetry-breaking without the 4a0 order.

The new experiment on KV3Sb5 also challenges the novelty of this work, in which the impact of the 4a0 order on the superconductivity is extinct. In terms of novelty, my concerns are: 1. Observation of various types of CDW order in a single compound is not rare in solids. Several transition-metal dichalcogenides (like NbSe2, TaS2) show CDW orders (even with superconductivity) which could also be tuned by temperature or other experimental probes. 2. The current work indeed reveals a cascade of correlated electron states. But I still could not directly learn the interplay between the CDW orders and superconductivity or band topology from this work.

At this point, I will leave the editor to decide whether the novelty of this work meets the standard of Nature or not.

Referee #2 (Remarks to the Author):

In the reply and the revised manuscript all my previous comments have been satisfactorily addressed. I recommend the publication of this work.