Peer Review File

Manuscript Title: Axial Higgs Mode Detected by Quantum Pathway Interference in RTe3

Reviewer Comments & Author Rebuttals

Reviewer Reports on the Initial Version:

Referees' comments:

Referee #1 (Remarks to the Author):

The manuscript entitled "Axial Higgs mode detected by Quantum Pathway Interference in RTe3" presents angle-dependent Raman scattering study of the charge-density-wave amplitude modes, named Higgs mode, in GdTe3 and LaTe3. The authors report a symmetry-breaking of the amplitudon mode behaviour (2-fold symmetry), compared to classical phonon modes which show a 4-fold symmetry. They ascribe this symmetry breaking to the nature of the amplitudon it-self, i.e. with an axial vector component, as described by a Raman vertex containing a “J_z” part. The experimental mechanism the authors claimed to be at play here relies on quantum interference between two intermediate Raman process (from bands to the same symmetry and from bands with orthogonal symmetries).

The conclusion reached by the authors are very interesting and clearly original, using indeed an experiment that does not require extreme conditions. The readership is possibly broad enough for the Nature journal. The data are of high quality. Nevertheless the analysis and description of the data needs to be improved further before the main conclusion of the manuscript can be reached.

- First, only the peak at 71 cm-1 is identified as a CDW mode by Chen et al. (at low temperature). And the manuscript seems to reach here the same conclusion. Nevertheless, the results point to at least 3 others modes between 7 and 11 meV that present a large intensity difference between the a’b’ and b’a’ configurations, so a 2-fold symmetry. The authors may present the angular dependence of the intensity of all the modes, clearly labelling them. And the conclusion on a 2-fold symmetry breaking may be characterized for each modes. If not only the CDW mode present the 2-fold symmetry, the author have to explain it to reach their main conclusion.

- The Raman vertex used in the manuscript do not match the ones of Hayes and Loudon. In the SI, the B1g vertex in D2h group has different coefficient (e, d), not being in a tetragonal structure. I suggest to use the correct Raman vertex, especially for the purpose of the paper that relies on symmetry argument. In general the fitting parameters have to be presented, compared between modes and commented.

- In Eiter at al. PNAS 110, 64 (2013), the authors report remarkable selection rules between aa and cc configurations in ErTe3. An enhancement of the Raman vertices by two order of magnitude is reported along one or the other diagonals (as the Q vectors), due to lifted degeneracy by hybridization. This process then gives rise to a 2-fold symmetry (aa≠cc). Could this process apply to the present systems with proper treatment of the Fermi surface reconstruction and then explain the 2-fold apparent symmetry? Could you provide the Raman vertex calculations for the two systems?

- Fig 2 is not clear in general: What is “Diagonal”? c) symmetric process is not presented contrary to the caption claims. Explain what the presented angle is.

- It is not clear how the resonance response combine with the angular momentum change. A full calculation of the interference terms should be provided in the SI.

Some additional comments:

- l.99: “the phonon of the phonons” needs to be corrected as well as the rest of the sentence.

- l. 123: please clarify the claim: “out fits… reveal the symmetric, off-diagonal terms are nearly-zero”

- In the SI, the Ag Raman vertex (p.7) has “d” elements that are not generally required in D2h group. The authors may clarify how they justify inserting these new Raman element. Note also that the last element on the diagonal is nonzero for the Ag vertex.

- P. 9 of SI: the determination of the fitting parameters is confusing; what means x-data, y-data. In all the figures with such fittings, the parameters must be provided.

- All the figures with some spectra, please provide the angle of measurements.

- Fig S5: a) Ag modes cannot have a zero at 0° in XX. Please check.
b) what are the parameters?
c) at 0° in XX, the Raman vertex must be equal to zero. Some confusion in these figures.
d) to f) Are they all Ag modes? The XX data point are turned by 45° for f). It is surprising.

- Fig S6: Why the data are turned by 90° in XY configuration compared to Fig 3? Is it real? If so, could the authors explain the origin? What are the “same fitting parameters” and “differing model”?
-
- For a broad readership, the analogy with High energy physics deserves to be better described. What is an axial vector Higgs boson? Which Standard model extension requires its existence? Why is it interesting?

- Finally, I suggest to use the common space group name, ie. Cmcm.

Referee #2 (Remarks to the Author):

The manuscript "Axial Higgs Mode Detected by Quantum Pathway Interference in RTe3" provides the experimental evidence of the axial nature of the so called "Higgs mode" in the charge-density-wave (CDW) systems RTe3, with R=La,Gd. Exploiting the high values of the critical temperature for the CDW ordering in RTe3 (>380K), the authors perform ordinary Raman scattering at room temperature, well inside the CDW phase, considering different polarizations of the incident probe and of the detected light. First, the authors consider the parallel configurations: aa,bb,a'a', where "a" and "b" are the in-plane crystallographic axes and a'=a+b, b'=a-b. In this configuration, the Raman spectra clearly display the CDW Higgs mode, represented by a dumped resonance peaked around 5-6meV, below the Ag and Bg phonon modes. Remarkably, when considering the crossed configurations, a'b' and b'a', the Higgs mode is clearly observed in the a'b' configuration, while its intensity gets strongly suppressed in the b'a' geometry. The authors justify this anomalous behavior by exploiting the properties of the Raman tensor associated to the CDW Higgs mode. As the authors stress, the CDW Higgs mode allows for a photon incident in the direction "a" to be scattered not only in the same direction, but also in the direction "b". This is a consequence of the presence of two different CDW vectors: b*-q_CDW, which triggers the parallel scattering, and q_cdw, which triggers the crossed scattering. As a consequence, the Raman tensor of the CDW Higgs mode is not diagonal in the crystallographic basis. In addition, as the crossed scattering involves the change of the electronic angular momentum (from px to py or viceversa), the Raman tensor has an antisymmetric component. This implies that the excitation pathways interfere constructively in the a'b' geometry and destructively in the b'a' one. The resulting Raman intensity is suppressed in the b'a' geometry, as it is confirmed by the measured spectra, detecting the non-conventional axial nature of the CDW Higgs mode in RTe3.
In order to rule out secondary effects that could determine an anomalous Raman response beyond the axial Higgs mode in the GaTe3, as the intrinsic angular momentum of the Ga moments or the presence of a bidirectional CDW at lower temperatures, the authors analyze also the Raman response of LaTe3 (Tc>600K), which displays a much more conventional CDW than GaTe3, observing the same angular dependence of the Raman intensity of the Higgs mode as in LaTe3.
The measured Raman intensities are fitted by a model function that well reproduces the data.

The work presented in the manuscript and its results are quite original and of wide interest for the community of condensed matter Physics and not only. The experiment, the results and their interpretation are presented clearly and in great detail. It's worth appreciating that the experiment succeeds in unveiling an unconventional dynamical feature of the Higgs mode without the need to exploit perturbing spectroscopic techniques, which may involve e.g. intense electric fields boosting the system out of equilibrium. The use of the more controlled Raman scattering guarantees more fidelity to the results.
In my opinion, what is lacking in the manuscript for it to be published in Nature is a theoretical counterpart, meaning a simplified and purely qualitative model for the dynamics of the axial Higgs mode and for its coupling to the Raman probe, that can somehow describe the main experimental findings.
I have some remarks:
1) At line 38, "Nambu-Goldstein" should actually be texted as "Nambu-Goldstone";
2) In the matrix R_cdw (defined above the line 124): the elements (3,3) should be equal to g,

according to the supplementary material;
3) At line 132, the intensity I_b'a' should be: I_b'a'=|(e-f)-2d|^2, which in fact justifies the destructive interference;
3) The black lines in the Figs. 3A,3B should be green, according to what is denoted in the caption (and also at line 136);
4) The technical details provided in the supplementary informations are exhaustive and clearly presented. However, there is no informations about the errors statistic of the Raman intensities. In particular, it would be worthy to draw the error bars in the polar plots of the Figs. 3c-3e,4a-4d,S5,S6,S8, in order to understand how precisely the fitting model reproduces the measured data.

Referee #3 (Remarks to the Author):

Dear editor,

I'm reporting on the manuscript "Axial Higgs Mode Detected by Quantum Pathway Interference in RTe3" by Y. Wang et al.
First, let me state that I do fully support the publication of the present work. The authors have shown convincingly the unconventional nature of a CDW amplitude mode being of axial character in two systems GdTe3 and LaTe3.
The authors do show a very complete and comprehensive set of data and the manuscript is written extremely well. It is very clear for the reader following the line of thoughts and also the presentation of the data is is done (almost) perfectly clear. Probing the angle dependent Raman response of the CDW amplitude modes and their characteristic dependencies unambiguously show the unconventional nature of the amplitude response. An alternative scenario of internal atomic momenta the author do rule out by probing the response in the two different systems (R-La and Gd). Also sample characterisation is done very carefully to rule out spurious effects in the polarisation dependence from potential multiple domains etc.

The only part that I do not fully understand in the presentation of the amplitude modes dynamics is the temperature dependence. Why do the authors discuss the dependence of the amplitude mode but show the crossed response with the suppressed mode in Fig. 4e? What do I miss here or am I just confused?

However I do have one more important point, that does not reflect on the quality of the present work and on the results. I do understand that "Higgs" is becoming a hater topic these days due to advances of potential Higgs responses in superconductors. But starting from this point basically every amplitude mode becomes renamed "Higgs". The point is that in all these non superconducting systems no Anderson-Higgs mechanism is in place. And for "real" Higgs modes unfortunately in most cases the "extreme" conditions that the authors report on are still necessary (with exception of interplays of Higgs and CDWs or or renormalised Higgs modes) and are typically not found in simple Raman responses.
I am aware that not calling the amplitude mode Higgs steals some of a potential selling point since a lot of it bares also then similarities to phonon spectroscopy for CDWs and some is already done

using interference techniques on chiral phonons as the authors state in their introduction. But in particular in the framework of Higgs modes in superconductors the pollination dependencies are a key point to distinguish Higgs from potential other sources, among them CDW amplitude responses. Therefore I would suggest to be a bit more careful using "Higgs" and amplitude modes as the same thing.

Author Rebuttals to Initial Comments:

Manuscript ID: 2021-09-15087
Manuscript title: Axial Higgs Mode Detected by Quantum Pathway Interference in RTe_3

We would like to thank the referees for their very positive feedback, helpful questions and suggestions for improvement. As mentioned by referee 1: “The conclusion reached by the authors are very interesting and clearly original,... The readership is possibly broad enough for the Nature journal” referee 2 agrees stating: “The work presented in the manuscript and its results are quite original and of wide interest for the community of condensed matter Physics and not only. The experiment data are of high quality, the results and their interpretation are presented clearly and in great detail.” Similarly referee 3 comments: “First, let me state that I do fully support the publication of the present work...The authors do show a very complete and comprehensive set of data and the manuscript is written extremely well.” All three referees have also given very useful suggestions, especially the need to improve the theoritical components of the paper, better clarify the connection to high energy, and the use of the term axial Higgs. In accord with their suggestions we have made changes to the manuscript as detailed below. As such we believe the manuscript is now ready for publication in *Nature*.

Referee 1

The manuscript entitled "Axial Higgs mode detected by Quantum Pathway Interference in RTe3" presents angle-dependent Raman scattering study of the charge-density-wave amplitude modes, named Higgs mode, in GdTe3 and LaTe3. The authors report a symmetry-breaking of the amplitudon mode behaviour (2-fold symmetry), compared to classical phonon modes which show a 4-fold symmetry. They ascribe this symmetry breaking to the nature of the amplitudon it-self, i.e. with an axial vector component, as described by a Raman vertex containing a “J_z” part. The experimental mechanism the authors claimed to be at play here relies on quantum interference between two intermediate Raman process (from bands to the same symmetry and from bands with orthogonal symmetries).

The conclusion reached by the authors are very interesting and clearly original, using indeed an experiment that does not require extreme conditions. The readership is possibly broad enough for the Nature journal. The data are of high quality. Nevertheless the analysis and description of the data needs to be improved further before the main conclusion of the manuscript can be reached.

We are grateful to the referee for their positive response to our work. The referee is correct that the text could have better described the results and a more thorough analysis was needed to better justify our conclusions. Based on their feedback, the manuscript, analysis and theoretical approach has been substantially improved.

First, only the peak at 71 cm-1 is identified as a CDW mode by Chen et al. (at low temperature). And the manuscript seems to reach here the same conclusion. Nevertheless, the results point to at least 3 others modes between 7 and 11 meV that present a large intensity difference between the a'b' and b'a' configurations, so a 2-fold symmetry. The authors may present the angular dependence of the intensity of all the modes, clearly labelling them. And the conclusion on a 2-fold symmetry breaking may be characterized for each modes. If not only the CDW mode present the 2-fold symmetry, the author have to explain it to reach their main conclusion.

The referee raises a very important point. Firstly, we confirm that the the peak at 5.6 meV (45 cm^{-1}) at 300 K and close to 8.8 meV (71 cm^{-1}) at 8 K is an amplitude mode of the CDW. We have included the angular dependence for each peak as a polar plot in supplemental figure S6. To clearly show the Raman modes symmetries, we also made a table in the supplemental with all the Raman modes energies and symmetries. As mentioned by the referee, between 7 – 11 meV, beyond the low energy Higgs mode, some phonons have different intensities in a'b' then b'a' configuration. Specifically, we have 6 phonon modes between 7 – 11 meV. As shown in the polar plot in Figure S6 (reproduced below for ease) We have found that other than the Higgs mode, two phonon modes (one at 7.4 meV and another at 10.7 meV) also have a 2-fold symmetry in XY configuration. However these modes are finite q phonons that are folded in by the CDW. As such they can also undergo the same quantum interferernce as the Higgs mode.

We have 4 evidences for this conclusion:

1. These two modes disappear above the CDW transition temperature, see Eiter et al. PNAS 110, 64 (2013).

2. Similar to other Raman experiments: Lavagnini et al. Phys. Rev. B 81, 081101(R) and Chen et al. Appl. Phys. Lett. 115, 151905 (2019), we observe clear avoided crossing between these modes and the Higgs mode (shown in Fig. 4).

3. As shown by X-Ray scattering in Maschek et al. Phys. Rev. B 98, 094304 (2018), the Higgs mode is strongly mixed with these phonons.

4. As for other phonons modes at 7.7 meV, 9.3 meV and 9.9 meV, they show Bg symmetry from their angular dependence of the Raman susceptibility (see Fig.S6 and Table 1 in the supplemental, we also showed it here). As such they cannot couple with the Higgs mode.

To make this point clear, we also modified the main text paragraph 8 which now reads:

"Other than the CDW Higgs mode, the phonon modes at 7.4 meV and 10.6 meV also showed the intensity difference at a'b' and b'a' polarization. As previously established in X-ray measurement, the Higgs mode is strongly mixed with these phonons (Maschek, M. et al.Phys. Rev. B 98, 094304 (2018)) and they disappear above CDW transition temperature (Eiter et al. PNAS 110, 64 (2013)). (Details in supplemental Figure .S6)"

We also add the explanation above into supplemental fitting detailed section.

"As showed in Fig. S6, other than the CDW Higgs mode, there are two more modes that also have a 2-fold polarization dependence in XY channel. These two modes disappeared above the CDW transition temperature (Eiter et al. PNAS 110, 64 (2013)). In addition, similar to other Raman experiments: Lavagnini, M. et al. Phys. Rev. B 81, 081101 (2010) , we observe clear avoided crossing between these modes and the Higgs mode. Even in X-Ray scattering (Maschek, M. et al.Phys. Rev. B 98, 094304 (2018)), the Higgs mode is strongly mixed with these phonons. As for other phonons modes at 7.7 meV, 9.3 meV and 9.9 meV, they show Bg symmetry from their angular dependence of the Raman susceptibility (shown in Fig. S6). As such they cannot couple with the Higgs mode."

The Raman vertex used in the manuscript do not match the ones of Hayes and Loudon. In the SI, the B1g vertex in D2h group has different coefficient (e, d), not being in a tetragonal structure. I suggest to use the correct Raman vertex, especially for the purpose of the paper that relies on symmetry argument. In general the fitting parameters have to be presented, compared between modes and commented.

The referee is correct that for an orthorhombic structure the coefficients of the B1g mode are different. This is because the symmetry group allows for a unit cell with unequal sides, and, where the anisotropy determines the difference between the two coefficients. Hence, the B1g mode can generally have a symmetric and an antisymmetric component. However, in our system the ab plane is in fact nearly square with slight orthorhombic distortion in the direction of the CDW. For fitting the experimental data we indeed used the generic representation of the Raman tensor based on the orthorombic crystal symmetry group and found that the observed modes are consistent with a nearly tetragonal structure. Specifically, the antisymmetric component vanishes for the B1g modes (i.e. the off diagonal terms are equal). On the other hand, the amplitude mode does not follow this behaviour and develops a purely antisymmetric off-diagonal component, though here again the magnitudes are the same, consistent with nearly tetragonal structure. In the revised version of the manuscript, we highlight the symmetry constraints on the phonon modes and how these are contrasted with the amplitude mode.

Specifically, in the main text we added:

(i) in paragraph 8 *"in fitting the angular dependent Higgs mode susceptibility, we find that the off-diagonal symmetric terms (B_g vertex) are nearly zero."* to clarify that the amplitude mode has a purely antisymmetric component

(ii) in paragraph 11 *"In the supplemental material we extract the Raman tensor associated to each mode using a generic representation in the orthorombic crystal group where the parameters are optimized to best fit the experimental data. We find that both the A_g and B_g phonons follow the expected angular dependence with four fold modulation when the associated Raman tensor is purely symmetric, reflecting the fact that the structure is nearly tetragonal."* to clarify the expected Raman tensor for phonon modes.

Additionally, in the supplemental material we analyse each Raman mode and determine its frequency and symmetry. We use Voigt fittings to derive the angular dependence of each mode and compare to the theoretical predictions. Optimizing the parameters to fit the data, we find that phonon modes are purely symmetric, reflecting the nearly tetragonal structure of the material. On the other hand, the amplitude mode is found to have a purely antisymetric off-diagonal component, as well as a symmetric diagonal component, leading to the observed 2-fold symmetry with respect to the angle on incidence.

In Eiter at al. PNAS 110, 64 (2013), the authors report remarkable selection rules between aa and cc configurations in ErTe3. An enhancement of the Raman vertices by two order of magnitude is reported along one or the other diagonals (as the Q vectors), due to lifted degeneracy by hybridization. This process then gives rise to a 2-fold symmetry (aa≠cc). Could this process apply to the present systems with proper treatment of the Fermi surface reconstruction and then explain the 2-fold apparent symmetry? Could you provide the Raman vertex calculations for the two systems?

The referee is correct that the work by Eiter et al. captured the important mechanism by which the Higgs response is anisotropic when measured with parallel incident and scattered polarization. However the main focus was on non-resonant Raman scattering from the CDW gap and did not measure or account for the angular dependence. In particular, the antisymmetric component of the Higgs Raman response was not reported nor evident from the data or model used in that work. In contrast, we explicitly measure the polarization dependence of the CDW amplitude mode and reveal the axial property of the Higgs mode. Our study focuses on *resonant* Raman transitions and the angular dependence of the CDW *amplitude* mode, instead of *non-resonant* Raman transitions and the polarization dependence at *select* angles in the paper by Eiter et al. Nonetheless, the work by Eiter et al is a good starting point. In the supplemental material we extend the model developed in that PNAS paper, to include a finite Fermi energy; this reflects the electronic filling factor of our material and gives rise to the Fermi surface shown in Fig.1 of the main text (this is different from the Fermi surface of the model in the work of Eiter et al.). We analyse the resulting Fermi surface using a phenomenological model determined by the low energy Hamiltonian and find that we can generally separate the qualitative description into two regions: (i) regions where states are connected by the CDW and where the angular momentum does not change, and, (ii) regions where the orbitals are mixed due to next-nearest neighbour interaction and the CDW connects states with different angular momentum.

Furthermore, the previous calculations by Eiter et al., focused on the single-particle electronic Raman response. Here we further extend that by including the effect of an amplitude mode by modelling it as fluctuations on top of the CDW gap and calculate the Raman susceptibility from resonant processes involving an incoming photon and outgoing photon plus a Higgs mode. The lifted degeneracy from small but finite orbital mixing due to next-nearest neighbour interaction indeed enhances the scattering vertices around isolated points in the Fermi surface, as hinted in the work by Eiter et al. Importantly, these points satisfy the nesting condition $b^* - q_{CDW}$ set by the CDW, in this way enabling the Higgs mode to couple orbitals with different angular momentum. Calculating the intensity of scattered light for the cross-polarization configuration we find that depending on the chosen pathway it differs by a factor proportional to the mixing terms. In addition, in the revised version of the manuscript we clarify the importance of next nearest neighbour interaction and how the states on the Fermi surface depend on it by adding following text to paragraph 10:

"In the supplemental material we calculate the Raman susceptibility from resonant processes using a low energy model in the presence of a CDW gap and amplitude mode and find an asymmetric transition, depending on the chosen pathway. This asymmetry primarily comes from the points in the Fermi surface with nesting vector $b^* - q_{CDW}$ and is enhanced by the orbital mixing due to next-nearest neighbour interaction (Eiter et al. PNAS 110, 64 (2013))."

In the concluding paragraph we have added:

"Using a phenomenological description of the Fermi surface we elucidate the role of next-nearest neighbour interaction in the observed asymmetry of Raman transitions involving a change of angular momentum, though."

Additional details of the model and calculation are now provided in the revised supplemental in the section *"Model for the Raman susceptibility from the Amplitude Mode"*

Fig 2 is not clear in general: What is "Diagonal"? symmetric process is not presented contrary to the caption claims. Explain what the presented angle is.

The referee is correct that the text was not clear on this point. Here we intended to refer to responses for tensors that are purely diagonal and as such also purely symmetric. We note that a tensor with off-diagonal terms can have symmetric or antisymmetric components. The presented angle is the polarization rotation angle relative to the crystal a-axis. In Fig. 2 c-d, we fixed the caption to read :

"(c) Scattered Electric field resulting from Quantum interference of a diagonal (R_{ii}) and antisymmetric off-diagonal ($R_{ij} = -Rji$) Raman processes. (d) Scattered Electric field resulting from Quantum interference of a diagonal (R_{ii}) and symmetric off-diagonal ($R_{ij} = Rji$) Raman processes. The presented angle is the polarization rotation angle relative to the crystal a-axis."

To clarify this we have fixed the following sentences in main text:

"we would not observe any difference when swapping the incident and scattered polarization: in this case the cross-polarized Raman response has a four-fold angular symmetry, see Fig. 2d. However the indistinguishablity and thus pathway interference leads to the CDW intensity $I_{a'b'} = |(e-f)+2d|^2$ producing the constructive interference term and $I_{b'a'} = |(e-f)-2d)|^2$ the destructive interference term, and thus a purely two fold angular response in cross-polarized Raman, as shown in Fig. 2c). "

It is not clear how the resonance response combine with the angular momentum change. A full calculation of the interference terms should be provided in the SI.

First we would like to clarify that by resonance we refer to Raman scattering processes in which the incoming photon has energy producing purely real transitions. Using the electric dipole approximation, the resonant contributions to the Raman susceptibility can be separated into a symmetric and anti-symmetric part (Cardona, M. Light Scattering in Solids 1 (Springer Berlin Heidelberg, 1975)). The symmetric part can be represented as:

$$< f|\chi_{\mu\nu}|i >_S = (e^2/2m\omega_2 V)\sum_b\{[(E_b - E_i - \hbar\omega_1)^{-1} + (E_b - E_i + \hbar\omega_2)^{-1}] \cdot [< f|p_\mu(k_2)|b >< b|p_\nu(k_1)|i > + < f|p_\nu(-k_1)|b >< b|p_\mu(k_2)|i >]\}$$

and the anti-symmetric part is:

$$< f|\chi_{\mu\nu}|i >_{AS} = (e^2/2m\omega_2 V)\sum_b\{[(E_b - E_i - \hbar\omega_1)^{-1} - (E_b - E_i + \hbar\omega_2)^{-1}] \cdot [< f|p_\mu(k_2)|b >< b|p_\nu(k_1)|i > - < f|p_\nu(-k_1)|b >< b|p_\mu(k_2)|i >]\}$$

, where E_i is the scattering initial state ($|i\rangle$) energy, E_b is the intermediate state ($|b\rangle$) energy, and $|f\rangle$ is the final state. $\hbar\omega_1$, $\hbar\omega_2$ is the incident light and scattering light energy.

It is important to note that when ω_1 and ω_2 are small compared to the interband energies, the antisymetric part of the susceptibility tends to zero. However, if the photon energy is in the resonant range, the anti-symmetric part can show up and even become dominant. For our system, for the antisymmetric component to be present one requires an excitation with an axial symmetry, i.e., a mode with finite angular momentum.

As mentioned above, in the supplemental material we formulate an effective low energy theory and calculate the resonant contributions to the Raman susceptibility. We show that the orbital mixing arising from the residual next-nearest neighbor interaction allows the Higgs mode to couple states with different angular momentum and as a result induce a difference between the Raman spectra of the two pathways.

As for the interference, we mean the interference between the diagonal symmetric term and the off-diagonal anti-symmetric process shown in the main text, which results in the constructive and destructive interference of the Raman intensities with respect to the angle from the crystal a-axis (shown in fig.3). If we only had a purely antisymmetric Raman tensor, the resulting intensity would be strictly zero in XX and independent of angle in XY. Thus the angular momentum of the axial Higgs mode provides the antisymmetric components, while interference between quantum excitation pathways (symmetric and antisymmetric) results in the observed two-fold angular dependence in XY polarization.

To better clarify this we have modified the text describing the Raman response of the Higgs to read:

"This resonance combined with the angular momentum change induces a nonzero antisymmetric (i.e. $R_{ij} = -R_{ji}$) contribution to the Raman tensor (Cardona, M. Light scattering in solids 1 (Springer Berlin Heidelberg, 1975)), which by itself would produce a signal only in XY and not XX configurations. Ultimately it is the interference of this antisymmetric process with the symmetric, diagonal component that produces the two-fold response in the cross-polarized Raman."

Some additional comments:

- l.99: "the phonon of the phonons" needs to be corrected as well as the rest of the sentence.

We appreciate the referee pointing out this typo and have corrected this sentence as:

"The 5 meV broad peak is the CDW Higgs mode and all other sharp peaks are the phonons".

- l. 123: please clarify the claim: "out fits… reveal the symmetric, off-diagonal terms are nearly-zero"

We thank the referee for pointing out the details here were not clear. We have changed the sentence in the main text to read:

"In fitting the angular dependent Higgs mode susceptibility, we found the inclusion of the off-diagonal symmetric terms (B_g vertex) are nearly zero."

- In the SI, the Ag Raman vertex (p.7) has "d" elements that are not generally required in D2h group. The authors may clarify how they justify inserting these new Raman element. Note also that the last element on the diagonal is nonzero for the Ag vertex.

We agree with the referee. This is a typo and in our Ag colorplot fitting, we are still using D2h group and the off-diagonal d terms are zero. We also fixed the last diagonal term.

$$Ag = \begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

- P. 9 of SI: the determination of the fitting parameters is confusing; what means x-data, y-data. In all the figures with such fittings, the parameters must be provided.

We apologize for using this confusing terminology. x-data is the polarization angle data from 0 to 360 degrees, and y-data is the Raman susceptibility data calculated from Raman intensity for certain polarization angles. In the newer version, we directly use polarization angle and Raman susceptibility to avoid the confusion. We also added all the polar fitting parameter results for all the Raman modes in the Raman vertex format in the "Data Fitting Details" section of the supplemental as a table and changed the text to read:

"For Raman tensor data fitting, we fit the Raman susceptibility data calculated from Raman intensity as a function of polarization angle from 0 to 360 degrees(θ) for different Raman tensors."

- All the figures with some spectra, please provide the angle of measurements.

For figures with spectra, if it is in parallel channel(XX), aa is 0 deg, bb is 90deg and a'a' is 45 deg. But if it is in cross polarization channel(XY), ab is (XY 0^o), ba is (XY 90^o), a'b' is (XY 45^o) and b'a' is (XY 135^o). To make this clear, we modify the main text as:

"Here ab(XY 0^o) refers to the incident (scattered) light polarized along the crystal a(b)-axis. Similarly, a'b'(XY 45^o) represents the crystal rotated by 45 degrees from the ab configuration, where a' = a+b, b' = a-b. The 5 meV broad peak is the CDW Higgs mode and all other sharp peaks are the phonons."

We also modified Fig. 1 caption to read:

"The bottom plot is taken in cross linear polarization, for incident light aligned with the a'(45 degrees off the a-axis) direction and scattered light along b'(45 degrees from the b-axis) direction (green solid line). Upon swapping the incident and scattered polarization (dashed line), the response of all phonons modes is identical, while the amplitude mode is suppressed."

- Fig S5:

a) Ag modes cannot have a zero at 0° in XX. Please check.

b) what are the parameters?

c) at 0° in XX, the Raman vertex must be equal to zero. Some confusion in these figures.

d) to f) Are they all Ag modes? The XX data point are turned by 45° for f). It is surprising.

We are very sorry there was a mistake in the angle plotted in the original manuscript. In the newer manuscript version, we fixed the Ag, Bg plot angle mistake and made the polar plots for all the phonons in Figure. S5-6. We listed out all the fitting parameters for all the polar plots and we also made a table in the supplemental explaining the symmetry for each mode.

- Fig S6: Why the data are turned by 90° in XY configuration compared to Fig 3? Is it real? If so, could the authors explain the origin?

We thank the referee for pointing this out. We labeled the XX and XY wrong in the supplemental but this is fixed in the newer version.

What are the “same fitting parameters” and “differing model”?

We agree with the referee that this terminology is confusing. This is now cleared up in the "Data Fitting Details" section of the Supplemental, where "same fitting parameters" pertain to the Raman tensor elements for a given mode in both XX and XY, and the "different model" refers to the corresponding susceptibility representations polarization dependent function for the given mode, as calculated in this same section. We modified the supplemental text as:

“We constructed polar plots for individual angular dependent modes of Raman spectra in both parallel and cross linear polarization and fitted them accordingly to their particular Raman tensors. Crossed and parallel polarization configurations for a given phonon are analyzed and fitted simultaneously with the susceptibility model from different Raman tensors.”

- For a broad readership, the analogy with High energy physics deserves to be better described. What is an axial vector Higgs boson? Which Standard model extension requires its existence? Why is it interesting?

We agree with the referee that the term axial, may not be as familiar to the general audience, nor why the discovery of this new particle is interesting. Therefore we have modified the abstract to read:

“The elucidation of the anti-symmetric component via quantum pathway interference provides direct evidence that the Higgs mode contains an axial vector representation (i.e. a psuedo-angular momentum) and hints the CDW in $GdTe_3$ is unconventional.”

In addition we have added the following the text to the introduction:

“One example is the attempt to extend the standard model by enlarging the symmetry breaking. This results in additional particles, including a spin-1 Higgs boson, and dark matter candidates (Franzosi, D. B. et al. Journal of High Energy Physics 2016, 76 (2016)). Thus the detection of a Higgs mode with finite angular momenta (i.e. an axial Higgs) heralds the discovery of a heretofore undiscovered symmetry breaking and novel phase of matter.”

and changed paragraph 6 to read:

“Due to the orthorhombicity, these nesting conditions are not satisfied along the a-axis, resulting in a node in the CDW gap, suggesting an unconventional order. Similarly the requirement to change angular momenta when connecting the P_X to P_Y states with $b * -q_{CDW}$ suggests the Higgs mode has finite angular momenta. The interference between the two pathways associated with this mode, the possible axial nature of the Higgs, change in sign of the gap (i.e. p-wave order) and thus unconventional CDW order have yet to be explored theoretically or experimentally.”

- Finally, I suggest to use the common space group name, ie. Cmcm.

We prefer to use the bmmb group. Firstly, we can keep it the same as Lei at al. Science Advances, 6 (2020). In addition, we do ab plane back scattering. In general in Raman scattering and other experimental papers, the c axis is incoming light direction and along the van-der-Waals bond.

Referee 2

The manuscript "Axial Higgs Mode Detected by Quantum Pathway Interference in RTe3" provides the experimental evidence of the axial nature of the so called "Higgs mode" in the charge-density-wave (CDW) systems RTe3, with R=La,Gd. Exploiting the high values of the critical temperature for the CDW ordering in RTe3 (>380K), the authors perform ordinary Raman scattering at room temperature, well inside the CDW phase, considering different polarizations of the incident probe and of the detected light. First, the authors consider the parallel configurations: aa,bb,a'a', where "a" and "b" are the in-plane crystallographic axes and a'=a+b, b'=a-b. In this configuration, the Raman spectra clearly display the CDW Higgs mode, represented by a dumped resonance peaked around 5-6meV, below the Ag and Bg phonon modes. Remarkably, when considering the crossed configurations, a'b' and b'a', the Higgs mode is clearly observed in the a'b' configuration, while its intensity gets strongly suppressed in the b'a' geometry. The authors justify this anomalous behavior by exploiting the properties of the Raman tensor associated to the CDW Higgs mode. As the authors stress, the CDW Higgs mode allows for a photon incident in the direction "a" to be scattered not only in the same direction, but also in the direction "b". This is a consequence of the presence of two different CDW vectors: $b^* - q_{CDW}$, which triggers the parallel scattering, and q_{cdw}, which triggers the crossed scattering. As a consequence, the Raman tensor of the CDW Higgs mode is not diagonal in the crystallographic basis. In addition, as the crossed scattering involves the change of the electronic angular momentum (from px to py or viceversa), the Raman tensor has an antisymmetric component. This implies that the excitation pathways interfere constructively in the a'b' geometry and destructively in the b'a' one. The resulting Raman intensity is suppressed in the b'a' geometry, as it is confirmed by the measured spectra, detecting the non-conventional axial nature of the CDW Higgs mode in RTe3. In order to rule out secondary effects that could determine an anomalous Raman response beyond the axial Higgs mode in the GaTe3, as the intrinsic angular momentum of the Ga moments or the presence of a bidirectional CDW at lower temperatures, the authors analyze also the Raman response of LaTe3 (Tc>600K), which displays a much more conventional CDW than GaTe3, observing the same angular dependence of the Raman intensity of the Higgs mode as in LaTe3. The measured Raman intensities are fitted by a model function that well reproduces the data.

The work presented in the manuscript and its results are quite original and of wide interest for the community of condensed matter Physics and not only. The experiment, the results and their interpretation are presented clearly and in great detail. It's worth appreciating that the experiment succeeds in unveiling an unconventional dynamical feature of the Higgs mode without the need to exploit perturbing spectroscopic techniques, which may involve e.g. intense electric fields boosting the system out of equilibrium. The use of the more controlled Raman scattering guarantees more fidelity to the results.

We thank the referee for their positive response to our work. Indeed we agree that there are some details the needed to be better described in the text. We agree with the suggestion of the referee that improved theory and error analysis are important to make the conclusion more convincing. Based on these comments, we improved the data analysis and theoretical approach in this new version of manuscript.

In my opinion, what is lacking in the manuscript for it to be published in Nature is a theoretical counterpart, meaning a simplified and purely qualitative model for the dynamics of the axial Higgs mode and for its coupling to the Raman probe, that can somehow describe the main experimental findings.

In the new version of the manuscript we elaborate more on the relevant mechanisms that allow the amplitude mode to couple states with different angular momentum and how this manifests in the Raman intensities of the two pathways. Specifically, we have performed a new calculation, detailed in the supplemental material, where we model the material using a tight binding description, similar to the work by Eiter et al., PNAS 110, 64 (2013). We analyse the resulting Fermi surface using a phenomenological model determined by the low energy Hamiltonian and find that we can generally separate the Raman contributions into two regions: (i) regions where states are connected by the CDW and where the angular momentum does not change, and, (ii) regions where the orbitals are mixed due to next-nearest neighbour interaction and the CDW connects states with different angular momentum.

The effect of an amplitude mode is included in the dynamics by modelling it as fluctuations on top of the CDW gap. Using the textbook procedure of Feynmann diagrams, we calculate the Raman susceptibility from resonant processes involving an incoming photon and outgoing photon plus a Higgs mode. We find that the lifted degeneracy from small but finite orbital mixing due to next-nearest neighbour interaction enhances the scattering vertices around isolated points in the Fermi surface, as hinted in the work by Eiter et al. Importantly, these points satisfy the nesting condition $b^* - q_{CDW}$ set by the CDW, in this way enabling the Higgs mode to couple orbitals with different angular momentum. Calculating the intensity of scattered light for the cross-polarization configuration we find that depending on the chosen pathway it differs by a factor proportional to the mixing terms. All the calculation details are in supplemental section *"Model for the Raman susceptibility from the Amplitude Mode"*.

In addition to the changes in the supplemental material, in the revised version of the manuscript, we clarify how this treatment is in fact able to capture the relevant mechanism by which the amplitude mode couples states with different angular momentum and results in a difference of the Raman spectra between the two pathways by adding the following text to the abstract:

"The qualitative behaviour of the Raman spectra is well-captured by an appropriate tight-binding model including an axial Higgs mode."

and in paragraph 10:

"In the supplemental material we calculate the Raman susceptibility from resonant processes using a low energy model in the presence of a CDW gap and amplitude mode and find an asymmetric transition, depending on the chosen pathway. This asymmetry primarily comes from the points in the Fermi surface with nesting vector $b * - q_{CDW}$ and is enhanced by the orbital mixing due to next-nearest neighbour interaction (Eiter et al. PNAS 110, 64 (2013))."

and we added the following to the concluding paragraph:

"Using a phenomenological description of the Fermi surface we elucidate the role of next-nearest neighbour interaction in the observed asymmetry of Raman transitions involving a change of angular momentum."

I have some remarks: 1) At line 38, "Nambu-Goldstein" should actually be texted as "Nambu-Goldstone";

We thank the referee for pointing out this typo and we fixed it.

2) In the matrix Rcdw (defined above the line 124): the elements (3,3) should be equal to g, according to the supplementary material;

We fixed these matrices

3) At line 132, the intensity Ib'a' should be: $Ib'a' = |(e-f)-2d|^2$, which in fact justifies the destructive interference;

Indeed the referee is correct and we have fixed this typo.

3) The black lines in the Figs. 3A,3B should be green, according to what is denoted in the caption (and also at line 136);

We changed the line color and now it matches the captions.

4) The technical details provided in the supplementary informations are exhaustive and clearly presented. However, there is no informations about the errors statistic of the Raman intensities. In particular, it would be worthy to draw the error bars in the polar plots of the Figs. 3c-3e,4a-4d,S5,S6,S8, in order to understand how precisely the fitting model reproduces the measured data.

We apologize that a proper error analysis was not originally presented. In part this was originally omitted due to the excellent signal to noise. Nonetheless, we have added the error-bars to all of our polar plot figures. In many of the figures, the error is smaller than the data point size and thus is not visible. As all of our errors are smaller than the data dot size in the main text, we didn't explicitly show it, but it is included in supplemental Figure. S6.

We also modified the main text as: *"we plot the intensity versus crystal angle for representative phonons of A_g and B_g symmetry alongside the response from the Higgs mode (Fig.3c–e). The fitting details and error calculations are in the supplemental."*

We have also added the following to the supplemental section "Data Fitting Details" to clarify how the error was calculated: *"We use Voigt function to fit 3 independent spectra and then take the squared 2-norm of the residual as: error =* $\sum[fun(\theta)-\chi(\theta)]^2$*. Our error is the square root of this summation for each peak."*

Referee 3

I'm reporting on the manuscript "Axial Higgs Mode Detected by Quantum Pathway Interference in RTe3" by Y. Wang et al. First, let me state that I do fully support the publication of the present work. The authors have shown convincingly the unconventional nature of a CDW amplitude mode being of axial character in two systems GdTe3 and LaTe3. The authors do show a very complete and comprehensive set of data and the manuscript is written extremely well. It is very clear for the reader following the line of thoughts and also the presentation of the data is is done (almost) perfectly clear. Probing the angle dependent Raman response of the CDW amplitude modes and their characteristic dependencies unambiguously show the unconventional nature of the amplitude response. An alternative scenario of internal atomic momenta the author do rule out by probing the response in the two different systems (R-La and Gd). Also sample characterisation is done very carefully to rule out spurious effects in the polarisation dependence from potential multiple domains etc.

We thank the referee for their very positive review of our work and helpful suggestions.

The only part that I do not fully understand in the presentation of the amplitude modes dynamics is the temperature dependence. Why do the authors discuss the dependence of the amplitude mode but show the crossed response with the suppressed mode in Fig. 4e? What do I miss here or am I just confused?

Our primary goal in Fig. 4e is to confirm that we measure a temperature dependence consistent with previous experiments. Specifically, similar to other Raman works: Lavagnini et al. Phys. Rev. B 81, 081101(R) and Chen et al. Appl. Phys. Lett. 115, 151905 (2019), we observe a clear avoided crossing between the Higgs mode and the phonon modes at 7.4 meV and 10.7 meV. As shown by X-Ray scattering in Maschek et al. Phys. Rev. B 98, 094304 (2018), the Higgs mode is strongly mixed with these phonons. This is consistent with the notion that the Higgs mode should only couple with phonons of similar symmetry. Indeed as shown in the supplemental (Fig. S6), these phonons posses a 2-fold symmetry in XY polarization as they are finite q modes folded in by the CDW and thus can undergo the same quantum pathways.

As for other phonons modes at 7.7 meV, 9.3 meV and 9.9 meV, they show Bg symmetry from their angular dependence of the Raman susceptibility (see Fig. S6, reproduced above). As such they cannot couple with the Higgs mode. This is already been seen in Chen. Y et al. Applied Physics Letters 115, 151905 (2019) and Yusupov, R etal. Phys. Rev. Lett.101, 246402 (2008).

To better clarify these points we have modified the relevant paragraph in the main text to read:

"In addition, the Higgs mode displays an avoided crossing with the 7.4 meV phonon consistent with it revealing the the same symmetry as the Higgs (see supplemental Fig. S6). This is due to the fact that this mode is folded to $q = 0$ by the CDW and thus can undergo the same quantum pathway interference (Lavagnini, M. et al. Phys. Rev. B 81, 081101 (2010), Chen, Y. et al. Applied Physics Letters 115, 151905 (2019), and Maschek, M. et al.Phys. Rev. B 98, 094304 (2018).)."

However I do have one more important point, that does not reflect on the quality of the present work and on the results. I do understand that "Higgs" is becoming a hater topic these days due to advances of potential Higgs responses in superconductors. But starting from this point basically every amplitude mode becomes renamed "Higgs". The point is that in all these non superconducting systems no Anderson-Higgs mechanism is in place. And for "real" Higgs modes unfortunately in most cases the "extreme" conditions that the authors report on are still necessary (with exception of interplays of Higgs and CDWs or or renormalised Higgs modes) and are typically not found in simple Raman responses. I am aware that not calling the amplitude mode Higgs steals some of a potential selling point since a lot of it bares also then similarities to phonon spectroscopy for CDWs and some is already done using interference techniques on chiral phonons as the authors state in their introduction. But in particular in the framework of Higgs modes in superconductors the pollination dependencies are a key point to distinguish Higgs from potential other sources, among them CDW amplitude responses. Therefore I would suggest to be a bit more careful using "Higgs" and amplitude modes as the same thing.

The referee raises an significant and subtle point. One which requires some care and cannot be fully addressed in our manuscript. Despite the limited space, it is important to make readers aware of this subtly and thus we have added the following sentence to the introduction:

"In a superconductor the inclusion of electromagnetism results in a gaping of the phason or giving mass to the W and Z bosons of the electroweak theory. However this Anderson-Higgs mechanism leaves the amplitude mode largely unchanged, and thus by convention it is often referred to as the Higgs boson(Shimano, R. et al. Annual Review of Condensed Matter Physics 11, 103–124 (2020), Podolsky, D.et al. Physical Review B 84, 174522 (2011) and Pekker, D. et al. Annual Review of Condensed Matter Physics 6, 269–297 (2015))."

This sentence is based on the fact that the symmetry being broken in the standard model is believed to be the same as in superconductors, namely gauge symmetry; whereas in a charge density wave translational symmetry is broken. For superconductors this results in a gapping of the Nambu-Goldstone mode via the Anderson-Higgs mechanism. While in the standard model this gives rise to the W and Z boson's having mass, the amplitude mode (or Higgs boson) is mostly unaffected, with the exception of its lifetime. In a superconductor the difficulty in detecting the Higgs boson arises from the fact that variations in the amplitude in time do not linearly couple to electro-magnetic probes. However we do not judge whether a mode in a superconductor is Higgs based on its coupling to experimental probes, indeed the impressive nonlinear experiments are quite distinct from the efforts required in particle physics. The crucial question is whether the condensed matter analogue is meaningfully simulating its high energy counter part. Indeed the Higgs boson is ultimately a fluctuation of the amplitude of a spontaneously broken symmetry. In cases where it is scalar, this results from the manner in which the continuous symmetry is broken (i.e. just gauge and no other symmetries). For example the Higgs boson in the cuprate's is predicted to have a non-scalar component, yet is similarly difficult to detect as those in s-wave counter parts (e.g. Phys Rev B 87, 054503 (2013), Nat Commun 11, 287 (2020)). Thus since the amplitude mode, other than the method by which it is detected, results from the same general physical concept, we believe it is reasonable to call it a Higgs boson. We also note that we are not alone in this opinion, this has been used in a variety of papers in both condensed matter and cold-atoms, see for example: Nature 487, 454 (2012); Phys Rev B 102, 014102 (2020), Nature Physics 13, 638 (2017), Science Advances 5, eaaw5639 (2019), Science Advances 4, aap8652 (2018), Nature Materials volume 18, pages 563–567 (2019).

Additional changes

In addition to our changes made to address the questions and comments of the referees we have also made minor changes to improve the clarity of the manuscript. This include:

(i) Paragraph 4: "The Bloch bands near the Fermi energy are mainly composed of the P_X and P_Y orbitals of the tellurium sheet (Fig. 1b) as the P_Z orbital is much lower in energy. Since the RTe_3 slab is less densely packed within the ab plane, the chosen unit cell (c.f., Fig. 1a) results in the Fermi surface shown in Fig.1c, where hybridization between the two orbitals happens only at isolated points due to next-nearest neighbour interaction (Eiter et al. PNAS 110, 64 (2013))."

(ii) Fig.1(c): Used the correct color plot and momentum axes labels of the Fermi surface.

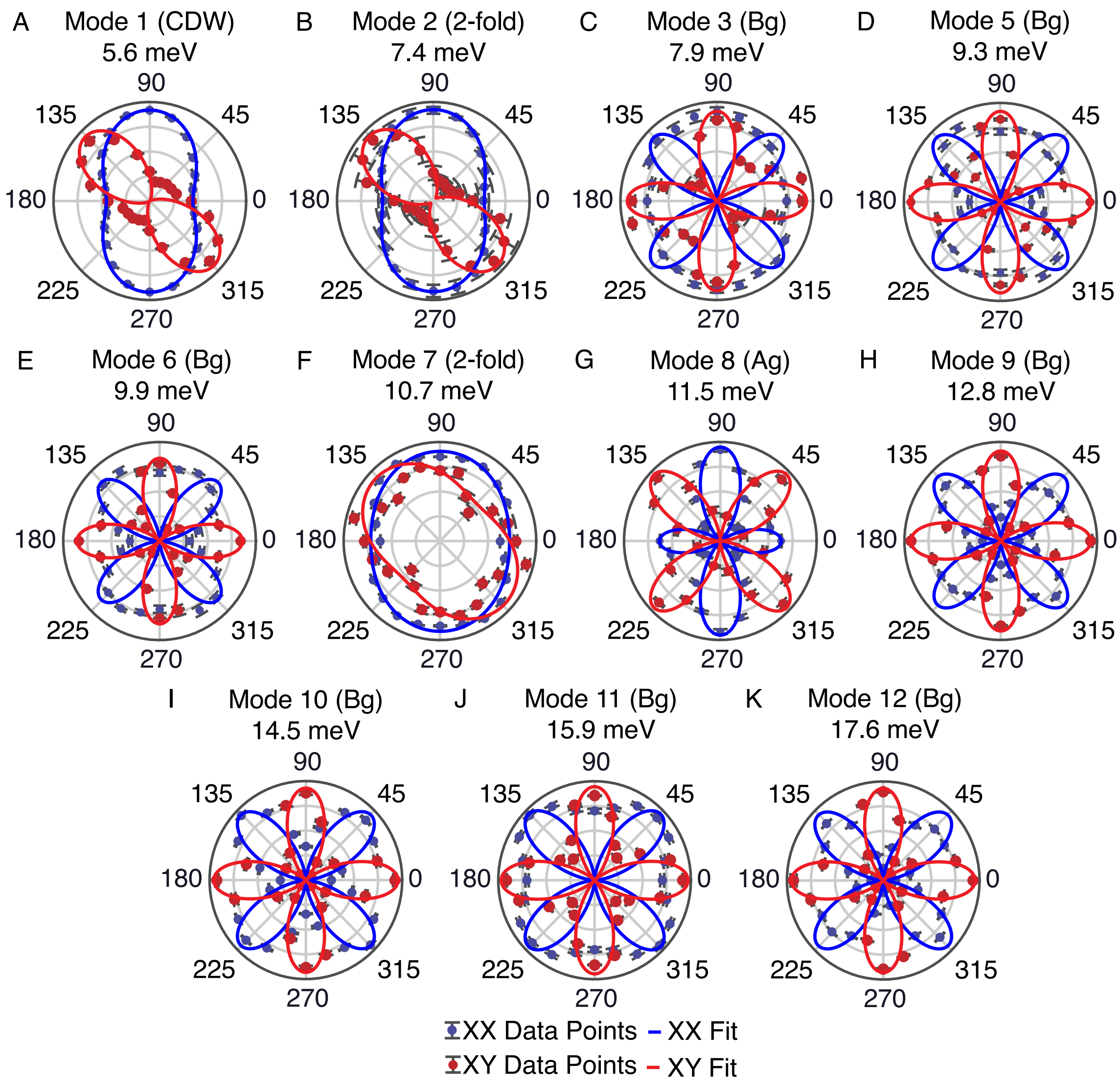

Figure 1: Experimental modes and polar fits for each $GdTe_3$ (532nm incident wavelength) mode at 300K using respective model functions (CDW, Ag, Bg). Mode 4 is excluded as the signal is too weak to accurately determine its' angular dependence. Fits were done using the same Raman tensor fitting parameters in XX and XY with corresponding model functions for Raman intensity in XX (orange) and XY (blue) polarizations, respectively.

Reviewer Reports on the First Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

The manuscript has been well-improved, with a phenomenological calculations included and all the fits and their parameters provided. It is explained why the low-energy modes (at 7.4 and 10.7 meV) also have a 2-fold symmetry because of their mutual coupling with the amplitude mode.

Nevertheless, thanks to the presentation of the angular dependences of all the modes, a major issue appears, which may question the main conclusion of the manuscript. Indeed, as shown Fig. S6, the modes at 7.9meV, 9.3 meV, 9.9 meV exhibit clear 2-fold symmetry in the XX polarization, with a shape similar to what is reported for the amplitude mode. The mode at 7.9 meV presents an almost fully symmetric angular dependence in XX polarization. The mode at 15.9 meV presents a 4-fold behaviour but without the zero expected at 0° and 90° and equivalent. All these modes are measured in the Bg symmetry. The Bg Raman vertex in the D2h group forces zero at 0 and 90° in XX polarization, whatever the orthorombicity is taken into account or not.

So the claim that only the Ag amplitude mode (and coupled ones) present unusual behaviour has to be corrected. It is possible that the striking effects on the Ag and Bg modes are related to the same mechanism. It has then to be explained before the main conclusion can be confirmed.

Besides two of mentioned Bg modes are present above the CDW transition and two are not. This questions the effect of the CDW transition on the polarization dependences. As a first check I would suggest to measure the polarization dependences above the CDW transition in the Gd-compound.

Therefore, with all the points I mentioned above, I cannot accept the publication of the manuscript in its present form. The main conclusion of this work is very interesting but it is not yet proven.

Here are some typos:
- pseudo-angular l33
- Symmetruc l142

Referee #2 (Remarks to the Author):

The manuscript has been considerably improved in the revised version. The theoretical part added to the supplementary information is very exhaustive. Then, I definitely recommend the manuscript for publication in Nature as it is.

Referee #3 (Remarks to the Author):

Dear editor,

going through the revised manuscript and detailed answers of the authors to the reports I am fully satisfied with response to the raised points. Also their thoughtful response to what is or could/should be called "Higgs" I can fully accept event though I do not fully share the same standpoint on what should be called "Higgs". But with their additional explanation the point of the authors is fully made clear and puts a clear distinction from the case of e.g. superconductors.

Thus I do fully support publication on the manuscript.

Author Rebuttals to First Revision:

Manuscript ID: 2021-09-15087
Manuscript title: Axial Higgs Mode Detected by Quantum Pathway Interference in RTe_3

We would like to thank the referees 2 and 3 for their recommendation to publish our manuscript. We also appreciate referee 1 noting: "The manuscript has been well improved" and that we have addressed all of their initial concerns. Referee 1 has raised a new criticism based on the additional data provided for the Raman response in XX polarization. Based on this we have more carefully analyzed the response for three phonons and explained the apparent inconsistency of another as an artifact of the analysis. Specifically we have found the original three modes reported are accidentally degenerate Ag and Bg modes. This explains the absence of zero intensity at angles where it is otherwise expected. In addition, this is consistent with the number and type of modes expected from group theory.

Furthermore, the new concern raised by referee 1 about our data taken in XX does not invalidate our main conclusion as we have focused on the analysis of XY data. Specifically, we did not aim to explain all anomalies in the Raman data, but rather focused on the amplitude mode. Indeed, even the referee does not provide any explanation as to how their concern would invalidate our conclusion, only that "it is possible that the striking effects on the Ag and Bg modes are related to the same mechanism." As we detail below, these are not striking, but rather a well known difficulty in fitting spectroscopic data when there is significant mode overlap. We provide a simple and straight forward explanation to the referee's concern, and thus feel strongly that the manuscript is now ready for publication in *Nature*.

The clarification of the data is now contained in the revised text of main and supplemental parts of the manuscript (marked in red). Our detailed response to the referee's concern is in blue. We also checked that the main text has fewer than 2700 words, as suggested by the editor.

Referee 1 (Remarks to the Author):

The manuscript has been well-improved, with a phenomenological calculations included and all the fits and their parameters provided. It is explained why the low-energy modes (at 7.4 and 10.7 meV) also have a 2-fold symmetry because of their mutual coupling with the amplitude mode.

We thank the referee for their description of the manuscript as well improved. We are also grateful for their careful reading of our work, which has helped to greatly improve it. The manuscript now contains a more complete description of all modes in the spectra.

Nevertheless, thanks to the presentation of the angular dependences of all the modes, a major issue appears, which may question the main conclusion of the manuscript. Indeed, as shown Fig. S6, the modes at 7.9meV, 9.3 meV, 9.9 meV exhibit clear 2-fold symmetry in the XX polarization, with a shape similar to what is reported for the amplitude mode. The mode at 7.9 meV presents an almost fully symmetric angular dependence in XX polarization. The mode at 15.9 meV presents a 4-fold behaviour but without the zero expected at 0° and 90° and equivalent. All these modes are measured in the Bg symmetry. The Bg Raman vertex in the D2h group forces zero at 0 and 90° in XX polarization, whatever the orthorombicity is taken into account or not.

We appreciate the referee pointing out the potential symmetry issue. **Symmetry is very important for this manuscript because our analysis is based on the anomaly in the XY response of CDW Higgs mode, not in XX**. Specifically, we saw 2-fold symmetry in CDW mode XY channel which has never been observed before. We then provided a reasonable explanation and justified it with phenomenological theory calculations. Other than the CDW Higgs mode and two phonons folded in by it, all the phonons behave normally in their XY polarization, showing 4-fold symmetry.

As XY was our main focus, we mistakenly overlooked the discprency in the XX behavior of some modes. We again thank the referee for pointing out this issue, which has led us to carefully check our fits and the raw spectra. As such we have realized the issue pointed out can be straightforwardly explained.

The main problem is the overlap of modes, the weak modes in the tail of stronger ones, accidental or near degeneracies. We begin with the mode at 9.3 meV. The referee mentioned this mode is Bg but shows 2-fold symmetry in parallel polarization. We thus looked more carefully at the spectra and found that at 0 or 90 °, this mode is merged into the CDW Higgs mode intensity and it is very hard to separate them (see original Figure 1 of the main manuscript and newly added Figure S8 in the supplemental that shows the individual fits, shown below for convenience). Indeed the apparent enhancement in XX is at the same angles where the amplitude mode is maximized. This is especially challenging as we do not have a precise model of the actual response of the amplitude mode and thus can only approximately fit it with a Lorentzian.

a

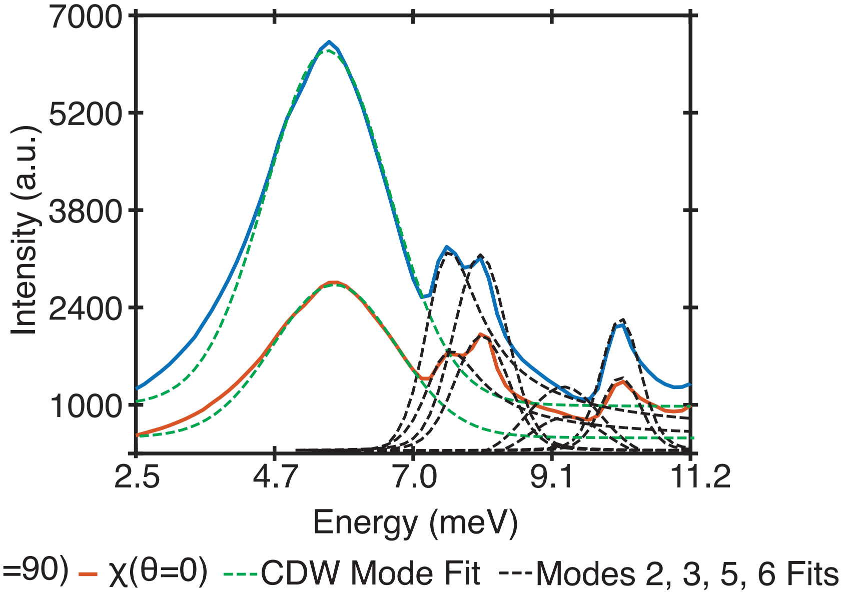

Figure S8 (a) GdTe3 Raman Spectra in parallel polarization for polarization angles of 0 degrees (orange) and 90 degrees (blue). Each spectra is accompanied by fits for individual modes to depict overlap, namely from CDW mode, resulting in Bg symmetry at 9.3 meV being difficult to detect.

For the 7.9, 9.9 and 15.9 meV phonon modes, the difference from the expected response of Bg modes is more subtle. Upon further examination we have concluded the spectra are the result of accidental or near degeneracies of Ag and Bg modes. This is most easily seen in the 15.9 meV mode. Since we originally fit the data with a single mode, the angular dependence is approximately the sum of the two nearly degenerate phonons. Indeed, the XX data appeared to have a 4 fold component on top of an angle independent component. This is consistent with two modes, one of Bg (four fold) and one of Ag symmetry with identical diagonal terms in the Raman tensor. In figure S7 in the supplemental (reproduced below for convenience), we demonstrate this by plotting response upon subtracting the 0 degree data, where the Bg component is zero. A second mode is clearly observed, consistent with two nearly degenerate modes.

To systematically demonstrate this mode is actually two nearly degenerate phonons, we fit the difference spectra, $\chi(15.9meV,\theta)$- $\chi(15.9meV,0)$, to extract the angular dependent mode paramaters for the Bg phonon. Next we fixed the Bg parameters and added a second mode to fit the original spectra at every angle. As shown in supplemental Figure S7, when added together the modes perfectly fit the spectra. Furthermore they reveal the expected behavior, namely a perfect four fold symmetry (Bg) and angle independent response (Ag) in XX. In addition, we found that the two modes are nearly degenerate (0.2 meV apart), as expected. Turning to the modes at 7.9 meV and 9.9 meV, we found that these appear to have an accidental degeneracy between one Ag and one Bg phonon. With this in mind, we first fit the XY intensity to a purely Bg mode. Next we simultaneously fit the XY and XX data using the Bg phonon combined with an Ag mode. The Bg mode parameters were kept fixed, while the Ag where allowed to vary.

The results are shown in Figure S7 in which a clear Ag component emerges in XX which proves considerably weaker in XY under the same tensor fitting parameters, explaining our nearly perfect 4-fold symmetry originally found in XY at 7.9 and 9.9 meV. We find these fits of degenerate modes perfectly describe the data.

As a last note, one may be concerned about the number of modes as compared to what is expected from group theory. Since two of the phonon modes are folded by the CDW (7.4 meV and 10.7 showing two-fold in XY as well), these are not to be counted in the prediction from group theory. As stated in the original manuscript, we expect 4 Ag modes and 8 Bg modes. However upon removing the two modes, previously assigned to Ag symmetry, we are now left with only 1 Ag mode and 8 Bg modes (taking into account the assumption that mode 5 (see supplemental) was too weak to discern clear symmetry and is to be considered Bg). If we include the three new modes that are accidentally or nearly degenerate (i.e. the Ag modes at 7.9meV, 9.9 meV and 15.9 meV), we now fully account for all modes expected with the proper symmetry. This lends additional strength to our argument that the apparent discrepancies are due to accidental or near degeneracies. Specifically that the angular dependent intensity results from two modes of different symmetries.

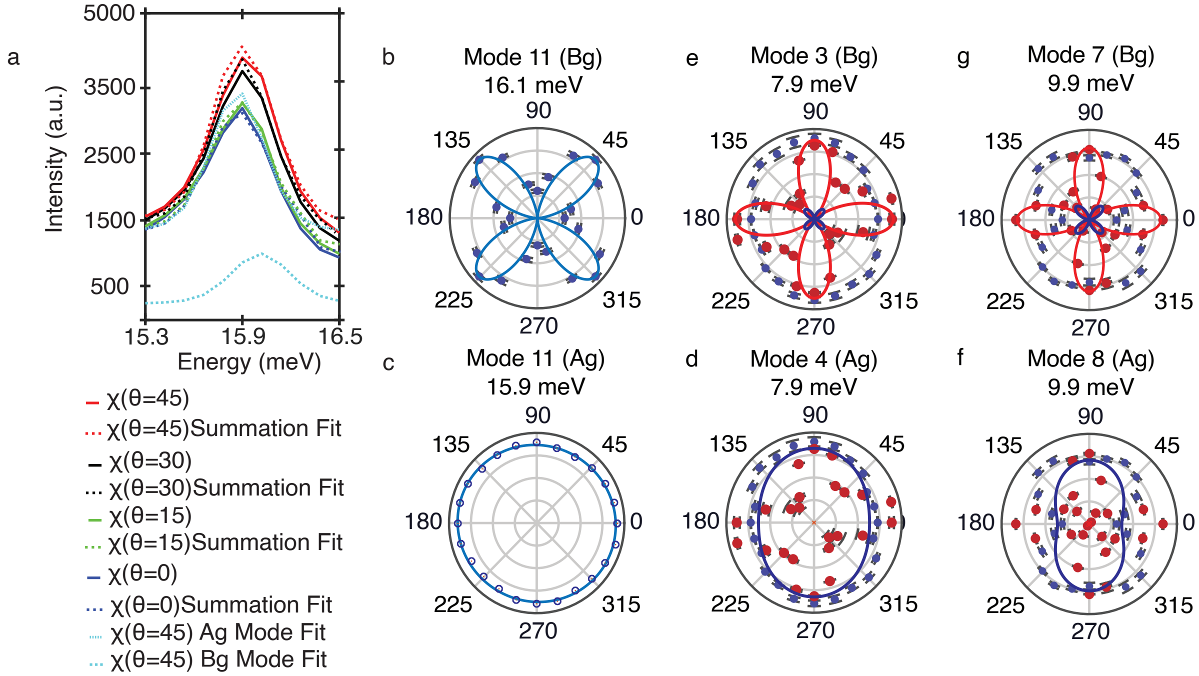

Figure S7 (a) $GdTe_3$ Raman spectra in parallel polarization for polarization angles 0, 15, 30, and 45 degrees (solid lines), near 15.9 meV. Each of these four spectra are accompanied by a summation of the fits for Ag and Bg modes present at 15.9 and 16.1 meV, respectively (dashed lines of same color). This summation is separated into Ag and Bg components for the 45 degree spectrum, shown in the light blue dashed lines. These reveal the presence of nearly degenerate Ag and Bg peaks. (b-e) Normalized XX and XY Raman suscpetibility for the 7.9, 9.9, 15.9, and 16.1 modes. Experimental results and polar fits for $GdTe_3$ Bg mode at 16.1 meV (b) and Ag mode at 15.9 (c). (d-e) Decomposition of mode at 7.9 meV into degenerate Ag and Bg components, showing accidental overlap of mode 3 and 4. (f-g) Decomposition of mode at 7.9 meV into degenerate Ag and Bg components, showing accidental overlap of mode 7 and 8.

To properly report these results, we have updated Figure S6 to indicate which modes are accidentally degenerate, show the new fitting results, as well as added the additional Ag mode at 15.9meV alongside the prior weaker Bg mode at 16.1 meV. We also modified the captions to indicate the new fitting (reproduced below for convenience).

Finally, we note that such an explanation cannot be applied to the two-fold behavior in XY, seen for the Higgs mode and the two modes folded in by the CDW. This behavior required an interference in the electric field, not a superposition in intensity. As such it is quite distinct from the degeneracies we report above. This further reinforces our assertion that the concern raised by the referee does not invalidate our original conclusion about the axial nature of the Higgs in RTe3.

So the claim that only the Ag amplitude mode (and coupled ones) present unusual behaviour has to be corrected. It is possible that the striking effects on the Ag and Bg modes are related to the same mechanism. It has then to be explained before the main conclusion can be confirmed.

As mentioned above, the anomaly of the CDW Higgs mode is in XY channel. For mode 2 (7.4 meV) and mode 9 (10.7 meV), they show 2-fold symmetry in XY polarization channel. However, for mode 3 (7.9 meV), mode 6 (9.3 meV) and mode 7 (9.9 meV), they show 4-fold symmetry as normal, which confirms the discrepancies in XX are unrelated to anomalous response of the Higgs mode. Furthermore as discussed above, the reason for an apparent 2-fold response in XX is either the strong overlap with the amplitude mode or the result of accidental or near degeneracy between two Ag and Bg modes. Nonetheless such degeneracy does not significantly affect the response in XY. We note that the problem of separately analyzing the response of nearly degenerate modes relevant to all of these in XX is well known. Nonetheless as this problem is not present in the XY configuration, upon which our main argument is based, this does not affect out main conclusion.

Besides two of mentioned Bg modes are present above the CDW transition and two are not. This questions the effect of the CDW transition on the polarization dependences. As a first check I would suggest to measure the polarization dependences above the CDW transition in the Gd-compound.

As described above the apparent anomalies are easily explained as resulting from mode overlap and are completely unconnected to the CDW. As such we do not believe any further data is required.

Therefore, with all the points I mentioned above, I cannot accept the publication of the manuscript in its present form. The main conclusion of this work is very interesting but it is not yet proven.

The main point of this paper hinges on data not criticized by the referee. Furthermore we have explained this as an unfortunate difficulty of analyzing nearly degenerate modes. We have modified the manuscript and supplemental to clarify this point as shown below.

Manuscript: Other than the CDW Higgs mode, phonons coupling with the CDW at 7.4 meV and 10.7 meV also showed an intensity difference between a'b' and b'a' polarization. As previously established, the Higgs mode is strongly mixed with 7.4 meV and 10.7 meV phonons and they disappear above the CDW transition temperature. Four other modes revealed responses in XX that appear different from what is expected by symmetry. However one of these modes (9.3 meV) strongly overlaps with the Higgs. As such it is hard to accurately extract its full angular dependence. For the modes at 7.9, 9.9 and 15.9 meV, we find their angular dependence is straightforwardly described by nearly or accidentally degenerate Ag and Bg phonons. Nonetheless, the angular dependence in XY polarization of the 7.9, 9.3, 9.9 and 15.9 meV phonon modes all behave as expected for Bg modes (4 fold symmetry). Thus their response does not affect our main conclusions about the amplitude mode (see supplemental

Supplemental: A close examination of Fig S6, reveals the XX angular dependence for the for the 7.9, 9.3, 9.9 and 15.9 meV phonon modes is not consistent with pure Bg symmetry. Upon further examination we have concluded the spectra are the result of accidental or near degeneracies of Ag and Bg modes. This is most easily seen in the 15.9 meV mode. Indeed, the XX data appeared to have a 4 fold component on top of an angle independent component. This is consistent with two modes, one of Bg (four fold) and one of Ag symmetry with identical diagonal terms in the Raman tensor. In Fig. S7, we demonstrate this by plotting response upon subtracting the 0 degree data, where the Bg component is zero. A second mode is clearly observed, consistent with two nearly degenerate modes.

To systematically demonstrate this mode is actually two nearly degenerate phonons, we fit the difference spectra: $\chi(15.9meV, \theta)$- $\chi(15.9meV, 0)$ to extract the angular dependent mode paramaters for the Bg phonon. Next we fixed the Bg parameters and added a second mode to fit the original spectra at every angle. As shown in Fig. S7, when added together the modes perfectly fit the spectra. Furthermore they reveal the expected behavior, namely a perfect four fold symmetry (Bg) and angle independent response (Ag) in XX. In addition, we found that the two modes are nearly degenerate (0.2 meV apart), as expected. Turning to the modes at 7.9 meV and 9.9 meV, we found that these appear to have an accidental degeneracy between one Ag and one Bg phonon. With this in mind, we first fit the XY intensity to a purely Bg mode. Next we simultaneously fit the XY and XX data using the Bg phonon combined with an Ag mode. The Bg mode parameters were kept fixed, while the Ag where allowed to vary. The results are shown in Fig. S7 in which a clear Ag component emerges in XX which proves considerably weaker in XY under the same tensor fitting parameters, explaining our nearly perfect 4-fold symmetry originally found in XY at 7.9 and 9.9 meV. We find these fits of degenerate modes perfectly describe the data.

In addition the signal for the mode at 9.3 meV is fairly weak and it strongly overlaps with the Higgs mode. This is shown in Fig. S8 which contains the individual fits of all low enegy modes in XX polarization. This makes is quite difficult to separate the response of this mode from the Higgs, producing an apparent anomalous angular dependence in XX.

As a last note, one may be concerned about the number of modes as compared to what is expected from group theory. Since two of the phonon modes are folded by the CDW (7.4 meV and 10.7 showing two fold in XY as well), these are not to be counted in the prediction from group theory (4 Ag modes and 8 Bg modes). However upon removing the two modes, we are now left with only 1 Ag mode and 8 Bg modes (taking into account the assumption that mode 5 was too weak to discern clear symmetry and is to be considered Bg). If we include the three new modes that are accidentally or nearly degenerate (i.e. the Ag modes at 7.9meV, 9.9 meV and 15.9 meV), we now fully account for all modes expected with the proper symmetry. This lends additional strength to our argument that the apparent discrepancies are due to accidental or near degeneracies. Specifically that the angular dependent intensity results from two modes of different symmetries.

Here are some typos: - pseudo-angular l33 - Symmetruc l142

We thank the referee pointing it out. All the typos are fixed.

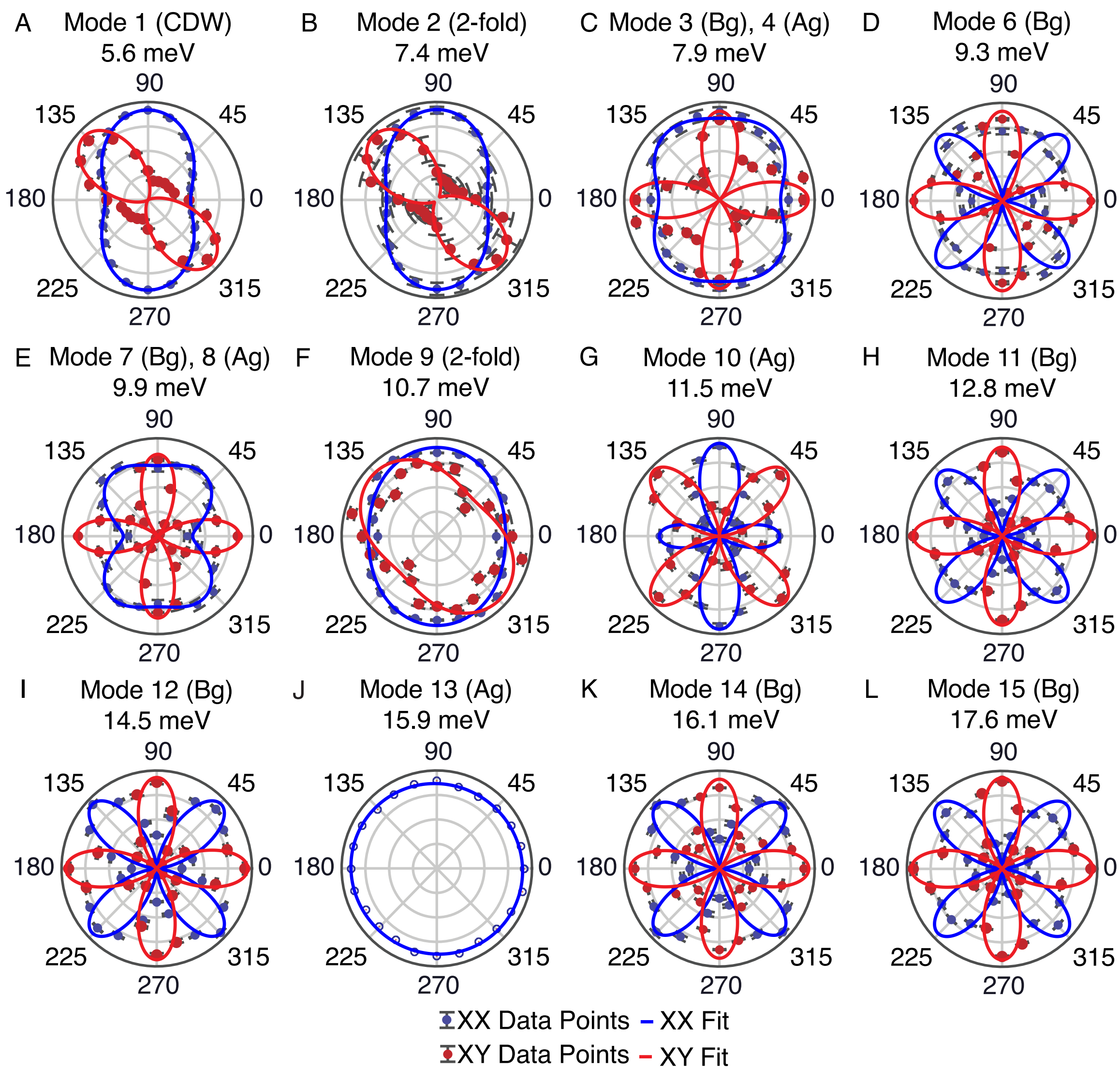

Figure S6: Experimental modes and polar fits for each GdTe3 (532nm incident wavelength) mode at 300K using respective model functions (CDW, Ag, Bg). Mode 5 is excluded as the signal is too weak to accurately determine its' angle dependence. Note mode 11 (Ag) is zero in cross-polarization and therefore is not shown. Also note that modes 3 & 4 and 7 & 8 are overlapping accidental and degenerate modes consisting of an Ag and a Bg mode each, the sum of which is plotted and fitted (see fig. S7 for individual Ag and Bg fits from these modes). Fits were done using same Raman tensor fitting parameters in XX and XY in corresponding model functions for Raman tensors in XX (blue) and XY (red) polarizations, respectively.

Reviewer Reports on the Second Revision:

Referees' comments:

Referee #1 (Remarks to the Author):

Report on the third version of the manuscript entitled "Axial Higgs mode detected by Quantum Pathway Interference in RTe3

The authors clarified the angular dependence of the Raman responses of the 4 surprising Bg modes in XY and XX polarization configurations. The mode at 9.3 meV is too weak and overlaps with intense modes, so the authors decided not to report the angular dependence. For the modes at 7.9 meV, 9.9 meV, and 15.9 meV, the authors extracted the presence of almost degenerate Ag modes for each of these Bg modes. This allows to present angular dependence expected from group theory for both the Bg and Ag modes. I think the presentation of the data, the analysis are well-improved and that the authors demonstrated fully their main conclusion. I am then happy to accept the manuscript for publication in Nature Journal.

Here are additional comments and suggestions:

Caption Fig S6: “Note mode 11 (Ag) is zero” -> mode 13

Figure S7: Show the response of mode 7 (Bg) in XX polarization

A final comment: The predictions of the positions of the modes in the CDW phase, which is now removed from the SI, will be very interesting to confirm the presence and positions of all the modes, including the degenerate ones.

Author Rebuttals to Second Revision:

Manuscript ID: 2021-09-15087
Manuscript title: Axial Higgs Mode Detected by Quantum Pathway Interference in RTe_3

Referee 1

The authors clarified the angular dependence of the Raman responses of the 4 surprising Bg modes in XY and XX polarization configurations. The mode at 9.3 meV is too weak and overlaps with intense modes, so the authors decided not to report the angular dependence. For the modes at 7.9 meV, 9.9 meV, and 15.9 meV, the authors extracted the presence of almost degenerate Ag modes for each of these Bg modes. This allows to present angular dependence expected from group theory for both the Bg and Ag modes. I think the presentation of the data, the analysis are well-improved and that the authors demonstrated fully their main conclusion. I am then happy to accept the manuscript for publication in Nature Journal.

We would like to thank the referees 1 for helping us to improve the manuscript.

To answer the additional comments and suggestions from referee 1

Caption Fig S6: "Note mode 11 (Ag) is zero" -> mode 13

We thank the referee pointing this out, we fixed the caption

Figure S7: Show the response of mode 7 (Bg) in XX polarization

We apologize for the confusion. We already plotted the mode 7 with the fittings in both XX and XY in Figure S7 (f and g). To make this clear we have now added a legend in the figure and also described it better in the caption. The specific change is below.

(d-g) Polar plots of XX(blue dots) and XY(red dots) polarizations for mode 3,4 and 7,8. (d-e) Experimental results and decomposition of the mode at 7.9 meV into degenerate Ag and Bg components, showing accidental overlap of mode 3 and 4. (f-g) Experimental results and decomposition of the mode at 9.9 meV into degenerate Ag and Bg components, showing accidental overlap of mode 7 and 8.

A final comment: The predictions of the positions of the modes in the CDW phase, which is now removed from the SI, will be very interesting to confirm the presence and positions of all the modes, including the degenerate ones.

The original calculation of the modes was based on the lattice structure without the CDW. As such we have found it does not have the accuracy to fully capture our results. This is especially true in light of the new modes we have found based on the Referee's feedback. The unit cell with the CDW is quite enormous and thus would require extreme resources to calculate by DFT or other methods. As this is not a central point in our paper, the modes we revealed are confirmed by other groups and methods, we choose to leave this for a future work.