nature portfolio

Peer Review File

Strong bulk-surface interaction dominated in-plane anisotropy of electronic structure in GaTe

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Please see the attachment.

Reviewer #2 (Remarks to the Author):

The authors present ARPES data and DFT calculations of GaTe, focussing on the material's surface electronic properties and its electronic anisotropy. The ARPES data of the surface of cleaved bulk GaTe is compared with DFT calculations of monolayer, bulk and a slab geometry, and is found to show best agreement with the slab calculations. The DFT calculations are then extended to analyse the effects of thickness on the electronic structure. Potassium doping of the system is also explored, both experimentally and theoretically.

Main comments

1. What is meant by bulk-surface interaction? There are several factors that may contribute. Do the authors mean surface reconstruction, genuine surface states, or effects due to dimensionality and/or confinement? Is this really an interaction between bulk and surface states? This is not very clear in the manuscript.

2. The separation between bulk and surface contributions in the slab model is not very clear. How has relaxation been achieved in the slab? The slab has two surfaces, so how do the "bulk-like" bottom five layers survive this relaxation and still represent bulk states? Similarly, how does the bottom surface affect the identification of surface and bulk states in Fig. 1? If the slab has been fully relaxed, then I would expect that a 7 layer slab only goes 3 layers into the bulk of the material.

3. Some essential information on the ARPES experiment is missing. What is the photon energy used, and what is the expected inelastic mean free path of the measured photoelectrons? Is the measurement performed on the surface of a cleaved bulk crystal? Or has some attempt to produce few-layer material been attemped? Has the photon energy been adjusted to confirm whether there is any out-of-plane dispersion, and whether these are surface or bulk states?

4. What is the purpose of the potassium doping experiments and calculations? It is not very obvious how this fits in with the rest of the study.

5. What is the potassium coverage in the experiments presented in Fig. 2? Some indication of the dopant concentration as a function of evaporation time is required to make claims of "heavy surface doping".

6. On page 8, the authors refer to bulk states and a bulk-surface interaction

for 3 layer GaTe. Such a system can hardly be considered as bulk-like.

Additional comments
7. Has the structure and stoichiometry of the source material been confirmed using any other methods, e.g. XRD?

8. What is the energy reference of the band calculations, i.e. why is the Fermi level not at the VBM or mid-point of the energy gap? Is there a band going to higher energy at a momentum not included in the displayed path?

9. Fig. 1b - it is difficult to see where the bulk symmetry points are. A guiding line connecting the points in 3D would be very helpful.

10. Fig. 1h has dots between G-Y and lines between G-X. It is easy to see the color of the lines along G-X, but very hard to follow these along G-Y.

11. Fig. 2 - is this really a binding energy scale? It looks like a kinetic energy scale.

12. In the discussion, the authors state that the anisotropy is the result of a strong bulk-surface interaction. This is misleading, since the anisotropy of the system is already established by the crystal structure. It may be more correct to say that the anisotropy is modified by the dimensionality of the system.

Reviewer #3 (Remarks to the Author):

In this manuscript, the authors report ARPES and first-principles band structure calculation studies of GaTe. By using ARPES, they have found strong anisotropy in the effective mass of valence-band dispersion, and concluded the importance of bulk-surface interaction to explain the contradicting ARPES data and band calculation. Although this work may be useful for understanding the evolution of overall band structure on GaTe from the bulk to the monolayer limit, I do not find any new physics and significance of the present study. Therefore, I do not recommend the publication of this manuscript in Communications Physics. This manuscript may be suitable for publication in more specialized journal. My specific comments are the following.

1) Observation of anisotropic band structure is not at all surprising, because it should be generally realized in many other systems. I do not understand why the authors put this anisotropy as a main issue of the present study.

2) The meaning of "bulk-surface interaction" is unclear. Such interaction would be limited to a very thin region (at most a few nm) and it would not play a role to control bulk-originated physical properties. If the authors want to say that it affects the band structure for a thin samples, they should show such an experimental evidence.

3) If the authors wish to discuss the bulk-surface interaction, they need to experimentally distinguish

the bulk and surface bands by performing the photon-energy-dependent ARPES experiments. Without the experimental identification of the bulk and surface bands and more sophisticated comparison between the experimental and calculated band structures, it would be difficult to discuss the nature of bulk-surface interaction.

4) ARPES data for the K-deposited samples tell us nothing. To show expected band shift due to the surface electron doping or surface band bending adds no new insights into the electronic states of GaTe.

5) Although the authors have calculated layer-dependent band structure and suggested the direct-indirect-direct transition, this transition is not supported by the experiment. Again, ARPES experiments for monolayer and a few layer GaTe samples would be necessary.

The authors describe the anisotropic character if the valence band of GaTe, making use of ARPES and first principle calculation. Despite the material could be potentially very interesting I do feel that this work needs major revision. In particular:

1) The manuscript is written in very poor English. It is extremely hard to follow.
2) The main topic discussed here is the anisotropy of the material and the manifestation of this in band structure measurements. Still, there are several reasons for anisotropy and this needs to be discussed. Is this related to lateral-confinement? What is the size-effect? Do the authors mean the effect produced by the reduction of the structures in size? This really needs to be clarified.
3) The authors talk about anisotropy in describing the VB structure of GaTe and the differences of the effective mass mx in GX and GY. Should not be this fully expected given the fact that the two points are inequivalent regardless of the bulk-surface interaction?
4) The authors mention a 1D dispersion along Gamma-X. I think this is very dangerous: not only I do not believe that the feature they observe is not 1D, indeed they should at least show a kz dispersion to prove that it is not 3d. But the data do not allow to see anything more than a smudge for the Fermi surface. Also, I believe that the strongly directional character of the Fermi surface can be simply given by a matrix elements argument. Which orbital form the VB structure? Which is the geometry of the instrument? How does this relate to the light polarisation used?
5) Matrix elements are necessary: the arguments about the spectral weight here and about that the top-valence band is weaker than the rest of the VB can be simply given by (a) kz broadening, (b) Photon energy used (c) polarisation

I would suggest the authors to do this sort of study before resubmission as it is crucial for interpreting photoemission spectroscopy data.

Dear Editor and Reviewers,

We are grateful to you and the referees for their earnest reviews of our manuscript. The current manuscript has already been modified according to the suggestions and comments from the referees. The detailed responses are listed below.

1. To highlight the topic of our work, the title of this paper has been modified to "Strong bulk-surface interaction dominated in-plane anisotropy of electronic structure in GaTe" in the revised manuscript.

2. The author information and contributions are updated in the revised manuscript. Hanwen Wang and Hongjian Wu have become our coauthors, who participated in the fabrication of the h-BN-encapsulated GaTe thin flakes and angle-resolved polarized Raman measurements, respectively. Hongen Zhu conducted more ARPES experiments on photon energy-dependent (k_z) and polarization-dependent measurements, thus his contribution is equal to the Kang Lai and Sailong Ju.

Reviewer #1:

The authors describe the anisotropic character if the valence band of GaTe, making use of ARPES and first principle calculation. Despite the material could be potentially very interesting I do feel that this work needs major revision. In particular:

1) The manuscript is written in very poor English. It is extremely hard to follow.

A1. We thank our referee for this rather straightforward comment. In light of this, we rewrote the manuscript not only according to the nice and reasonable scientific comments from our referees, we also spent time improving the way that we express our ideas and polishing the grammar throughout the manuscript. We hope this revised version can be easy to read and understandable to our referees, if possible, to other readers as well.

2) The main topic discussed here is the anisotropy of the material and the manifestation of this in band structure measurements. Still, there are several reasons for anisotropy and this needs to be discussed. Is this related to lateral-confinement? What is the size-effect? Do the authors mean the effect produced by the reduction of the structures in size? This really needs to be clarified.

A2. We thank our referee for pointing out this rather important concept issue which makes the topic of our manuscript become clear. In the revised manuscript, we have discussed several possible reasons that may result in the in-plane anisotropy of band structure in GaTe. Conventionally, the low-symmetry of the crystal structure determines the anisotropy of electronic structure in many anisotropic layered materials with black phosphorus as one of the typical examples. Here, the in-plane anisotropy of energy band dispersion will evolve in a way which will be independent of the layer thickness [Nat. Rev. Phys. 1, 306-317 (2019)]. Within this scenario, the in-plane anisotropy of hole effective mass calculated on the basis of monolayer GaTe shall be consistent with the one that extracted from the APRES spectra of GaTe bulk. However, our ARPES experiment demonstrates the hole effective mass along y direction is smaller than that along x direction in GaTe bulk, which is contradict to our theoretical result of monolayer GaTe. In addition, the VBM of GaTe bulk obtained by ARPES is located at $\bar{\Gamma}$, while that of monolayer is located at $\bar{X}$. These results indicate the in-plane anisotropic band structure of GaTe is not determined by the low crystallographic symmetry.

Previous study shows the infinitely extended bulk model could be used to interpret the ARPES spectra of black phosphorus [Nat. Nanotechnol. 9, 372-377 (2014)]. We then evaluate the validity of this model for GaTe. The PBE functional with and without considering the spin-orbit coupling effect are used to calculate the band structure of infinite extended bulk model, in which the highest valence band dispersion along x direction is stronger than that along y direction. This agrees with previous theoretical results [Phys. Rev. B 65, 115201 (2002), ACS

Nano 10, 8964-8972 (2016)], indicating the hole effective mass of the system for x direction is smaller than that for y direction, which is inconsistent with our experimental result. These results suggest that the bulk-surface interaction in the bulk with finite size might play an important role in the anisotropic electronic structure of GaTe. As shown in Fig.2c in the revised manuscript, the anisotropy of hole effective mass in 7-layer GaTe slab configuration which includes the bulk-surface interaction is in good agreement with the experiment.

When the number of layers increases from 8 to 30, both the in-plane lattice constant and band gap of the system converge to those of infinitely extended bulk model, while the in-plane anisotropy of hole effective mass of multilayer GaTe doesn't agree with that of the bulk model. This suggests the quantum confinement effect is not the reason for the in-plane anisotropy of band structure in GaTe. Therefore, the observed anisotropy of electronic energy bands originates from the strong bulk-surface interaction. Since the surface of a solid is a simple type of interface, the bulk-surface interaction can be also considered as a result of the interface effect.

3) The authors talk about anisotropy in describing the VB structure of GaTe and the differences of the effective mass mx in GX and GY. Should not be this fully expected given the fact that the two points are inequivalent regardless of the bulk-surface interaction?

A3. Thank you for the comments. Exactly as the reviewer said, the X and Y points in the surface BZ of GaTe are inequivalent due to the reduced crystalline symmetry within the plane of layer. However, the in-plane anisotropy of hole effective mass of the system without considering bulk-surface interaction such as monolayer GaTe is inconsistent with the experiment.

4) The authors mention a 1D dispersion along Gamma-X. I think this is very dangerous: not only I do not believe that the feature they observe is not 1D, indeed they should at least show a kz dispersion to prove that it is not 3d. But the data do not

allow to see anything more than a smudge for the Fermi surface. Also, I believe that the strongly directional character of the Fermi surface can be simply given by a matrix elements argument. Which orbital form the VB structure? Which is the geometry of the instrument? How does this relate to the light polarisation used?

A4. We thank our referee for pointing out this misleading statement in the manuscript. The original idea we aimed to state is the VB top along Γ-X is much less dispersive than that along Γ-Y which is the manifestation of band structure anisotropy. As mentioned by our referee, although the Fermi surface contour are relatively blurry, the spectral weight near E_F along Γ-X is almost featureless while only shows some intensity distributing along the Γ-X direction which is partly due to the small momentum range of the Brillouin zone. Here, we removed the word "one-dimensional" and revised the sentence as "The discrete feature for direction $\bar{\Gamma}$-$\bar{Y}$ and the continuous feature along direction $\bar{\Gamma}$-$\bar{X}$ evidence a stronger dispersion of the highest valence band along y direction than that along x direction." so that the description would become precise.

The band structures presented in Fig. 1(c) and (e) in the submitted manuscript (still retained in the revised version) were obtained by ARPES using a Helium discharge lamp as the photon source so that the capability of resolving different orbital contributions was lacking. Motivated by our referee, we conducted more ARPES experiments on synchrotron especially focused on photon energy-dependent (k_z) and polarization-dependent measurements. The photon energy-dependent measurements were carried out using photons ranging from 11 to 23 eV due to the limitation of the instruments, while this photon energy range is complementary to the earlier experiments [Phys. Rev. B 65, 115201 (2002)]. The ARPES intensity near E_F as a function of the momentum k_y as well as the probing photon energy is shown in Fig.S5. in the supplementary materials. The cross-section of the Fermi surface seems to be rather slender along the k_z direction, suggesting that the k_z dispersion is considerably weak. It is worthy to note that the measured k_z dispersion is less strong than expected from the calculations, which is consistent with the results reported before [Phys. Rev. B 65,

115201 (2002)]. Since the k_z dispersion is minor within our probing photon energy range, we chose photon energies which deliver strong signal intensity to perform the polarization-dependent measurements because the efficiency of s(LV) polarization is much lower than p(LH) polarization in the experimental apparatus.

The scheme of our polarization-dependent measurements is shown in Fig. 2(g) in the revised manuscript. The selection rule indicates that the p(LH) polarization should be sensitive to probe the p_z and p_x orbitals, while for the s(LV) polarization, the transition matrix element is detectable only for photoemission originating from p_y orbital. According to our theoretical calculations based on the 7-layer slab model that shown in Fig. 2(f), the VB top is dominated by the p_z orbital. Here, as we can see in Fig. 2(h), our measurements using p(LH)-polarized light yield stronger spectral weight for the VB top than using s(LV) polarization, moreover, the VB locates between -1.5 and -2 eV below E_F that also dominated by the p_z orbital is significantly more distinguishable when probing with p(LH)-polarization. As for VB surrounding the Γ point while locates at -1.0 eV and higher binding energies is dominated by p_x and p_y orbitals, these band features are both pronounced under different polarizations. The distinguishing spectral weight distributions between the two measurements illustrate that the VB top host a predominantly different orbital makeup compare to band structures reside at binding energies higher than -1.0 eV.

5) Matrix elements are necessary: the arguments about the spectral weight here and about that the top-valence band is weaker than the rest of the VB can be simply given by (a) kz broadening, (b) Photon energy used (c) polarization

A5. We thank our referee for all the comprehensive suggestions. The matrix elements analysis has been expounded in part 4.

Reviewer #2:

The authors present ARPES data and DFT calculations of GaTe, focussing on the material's surface electronic properties and its electronic anisotropy. The ARPES data of the surface of cleaved bulk GaTe is compared with DFT calculations of monolayer, bulk and a slab geometry, and is found to show best agreement with the slab calculations. The DFT calculations are then extended to analyse the effects of thickness on the electronic structure. Potassium doping of the system is also explored, both experimentally and theoretically.

Main comments

1. What is meant by bulk-surface interaction? There are several factors that may contribute. Do the authors mean surface reconstruction, genuine surface states, or effects due to dimensionality and/or confinement? Is this really an interaction between bulk and surface states? This is not very clear in the manuscript.

A1. We thank our referee for pointing out these important issues which makes the topic of our manuscript become clear. In this work, we find that the anisotropic energy bands obtained by ARPES couldn't be interpreted by the band structure of infinitely extended bulk model and monolayer GaTe. Only the bulk in combination with surface effect which includes bulk-surface interaction naturally could reproduce the experimental results. Since the surface of a solid is a simple type of interface, the bulk-surface interaction can be considered as a result of the interface effect.

The other possible mechanisms raised by the referee have been examined in our revised manuscript. It is easily to rule the surface reconstruction out since the GaTe possesses a dangling-bond-free surface. The genuine surface states are not found by experiment which is consistent with the early reported results [Phys. Rev. B 65, 115201 (2002)], also shown in Fig.S5 in the supplementary materials, the k_z dispersion is minor and our band structure calculation reveals highest valence band of GaTe is dominated by the bulk states. The effect of quantum confinement on the anisotropy of band structure also is discussed in the revised manuscript. The band structures of GaTe with the number of layers increasing

from 8 to 30 are calculated by PBE functional. As shown in Fig.S3 in the supplementary materials, the in-plane lattice constant and band gap of the system converge to those of infinite extended bulk model, while the in-plane anisotropy of hole effective mass of the system remains different with that of bulk model. This suggests the quantum confinement effect is not the primary mechanism for the in-plane anisotropy of band structure in GaTe.

2. The separation between bulk and surface contributions in the slab model is not very clear. How has relaxation been achieved in the slab? The slab has two surfaces, so how do the "bulk-like" bottom five layers survive this relaxation and still represent bulk states? Similarly, how does the bottom surface affect the identification of surface and bulk states in Fig. 1? If the slab has been fully relaxed, then I would expect that a 7 layer slab only goes 3 layers into the bulk of the material.

A2. Thanks for the comments. In the revised manuscript, the middle five layers of 7-layer slab model are fixed as the bulk region and the top and bottom one layer are regarded as the surface region. The atomic positions of surface are relaxed. The calculated band structure of 7-layer slab model is shown in Fig.2d in the revised manuscript, which shares the same features of band structures of 8-layer and 9-layer GaTe, as we can see in Fig.3(h-i) in the revised manuscript. This suggests the middle five layers of 7-layer slab model could represent the bulk region.

3. Some essential information on the ARPES experiment is missing. What is the photon energy used, and what is the expected inelastic mean free path of the measured photoelectrons? Is the measurement performed on the surface of a cleaved bulk crystal? Or has some attempt to produce few-layer material been attemped? Has the photon energy been adjusted to confirm whether there is any out-of-plane dispersion, and whether these are surface or bulk states?

A3. We thank our referee for reminding us to complement the experimental details of ARPES that seems to be insufficiently presented in the “MENTHODS”

part. All ARPES measurements were performed on the surfaces of bulk single crystals that cleaved in situ under UHV. The band structures shown in Fig. 1(c) and (e) in the submitted manuscript (still retained in the revised version) were obtained by ARPES using Helium discharge lamp (21.2 eV) as the photon source at Vacuum Interconnected Nanotech Workstation (NANO-X) so that the capability of resolving different orbital contributions was lacking. The potassium surface doping experiments along with photon energy-dependent (k_z) and polarization-dependent ARPES measurements (included in the revised manuscript) were conducted on Hefei Light Source.

The photon energy-dependent measurements were carried out using photons ranging from 11 to 23 eV due to the limitation of the instruments, while this photon energy range is complementary to the earlier experiments [Phys. Rev. B 65, 115201 (2002)]. The ARPES intensity near E_F as a function of the momentum k_y as well as the probing photon energy is shown in Fig.S5 in the supplementary materials. The cross-section of the Fermi surface seems to be rather slender along the k_z direction, suggesting that the k_z dispersion is considerably weak. It is worthy to note that the measured k_z dispersion is less strong than expected from the calculations, which is consistent with the results reported before [Phys. Rev. B 65, 115201 (2002)]. Furthermore, no obvious surface states have been observed in our experiments and nor in the earlier measurements [Phys. Rev. B 65, 115201 (2002)], the absence of dangling bonds at the GaTe surface shall play an important role in preventing the surface states from emerging.

In terms of the inelastic mean free path, it is unknown in GaTe a priori, to be precise, but it is presumably less than 1 nm if one takes the aforementioned photon energy range into account [Surf. Interface Anal. 1, 2 (1979)] which means the effective photoelectron signal comes from the very top layers of GaTe surface. However, this doesn't necessarily mean that the ARPES results we got solely represent the surface or the bulk, instead, our theoretical slab model shows the best agreement with the experimental results. This is the point that we run the story here. Certainly, some few-layer samples would be relatively more realistic,

there is also no doubt that the project will face more challenges over the course of the ARPES experiments, ie., some micro-ARPES even nano-ARPES equipment is needed which is beyond the reach of us at the present pandemic situation. In order to circumvent this dilemma, we fabricated a series of h-BN encapsulated GaTe thin flakes with different layer thickness and performed polarized Raman spectroscopy, here, the 3.53 and 4.87 nm GaTe thin flakes were identified by Raman mapping method that they both have close binding and thus the same in-plane orientation with the much thicker bulk part, respectively. The corresponding results are shown in Fig.S11 and Fig.S12 in the supplementary materials, in contrast to the early reported results that a monoclinic to hexagonal phase transition happens with the decreasing of the GaTe layer thickness [Small 17, 2007909 (2021), Phys. Chem. Chem. Phys. 18, 18719-18726 (2016)], our results demonstrate that the GaTe monoclinic phase is robust for the flake thickness down to 3.5 nm, this suggests the GaTe thin flake may be very sensitive to ambient conditions, while our calculations based on few layer GaTe slab model is quite rational.

4. What is the purpose of the potassium doping experiments and calculations? It is not very obvious how this fits in with the rest of the study.

A4. Thanks for the comments. Our first-principles calculations reveal the highest valence band is mainly occupied by the electrons from the bulk region, indicating that the surface doping wouldn't have an impact on the anisotropy of highest valence band. To further demonstrate this phenomenon, we measure and calculate the band structure of GaTe doped with potassium atoms. As the reviewer said, it doesn't fit the main topic discussed in this work and has been removed from the revised manuscript.

5. What is the potassium coverage in the experiments presented in Fig. 2? Some indication of the dopant concentration as a function of evaporation time is required to make claims of "heavy surface doping".

A5. We thank our referee for putting forward the monitoring of the potassium coverage at different stage which is of importance. Actually, this was done several times by measuring the K 3p core-level spectra, in the case of "heavy surface doping", we made the evaporation time longer enough (~14 min) until no further change to the band structure in the binding energy direction can be observed. However, considering the discussion of potassium doping to manipulate GaTe surface is straying from the main theme of this paper to a certain degree, we decided to remove this part and put in some more experimental results that of relevance, eg., photon energy-dependent and polarization-dependent ARPES measurements as well as layer-dependent Raman spectroscopy.

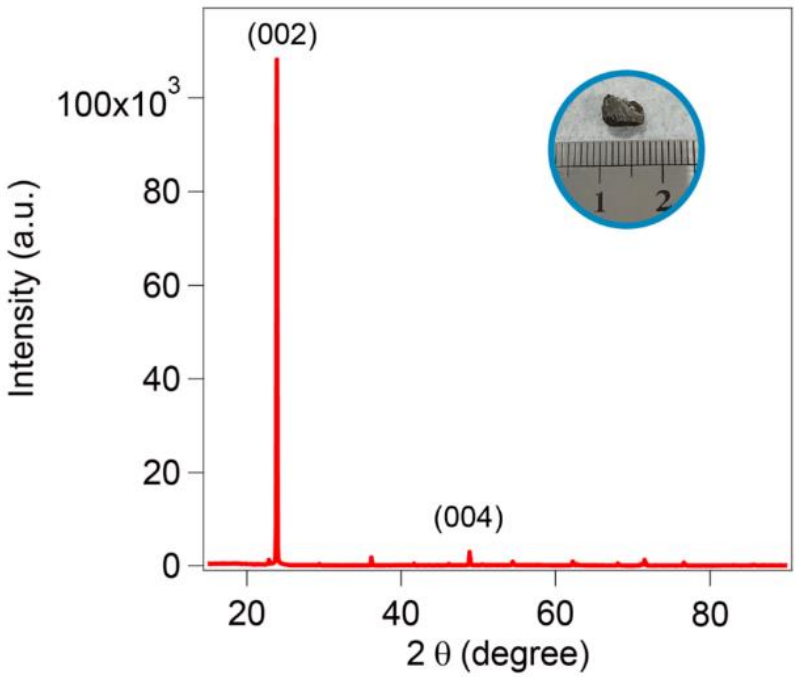
6. On page 8, the authors refer to bulk states and a bulk-surface interaction for 3 layer GaTe. Such a system can hardly be considered as bulk-like.

A6. Thanks for the comments. We agree with this point of view because the band structure of 3-layer GaTe is inconsistent with the ARPES spectra. This misleading statement has been removed from the revised manuscript.

Additional comments

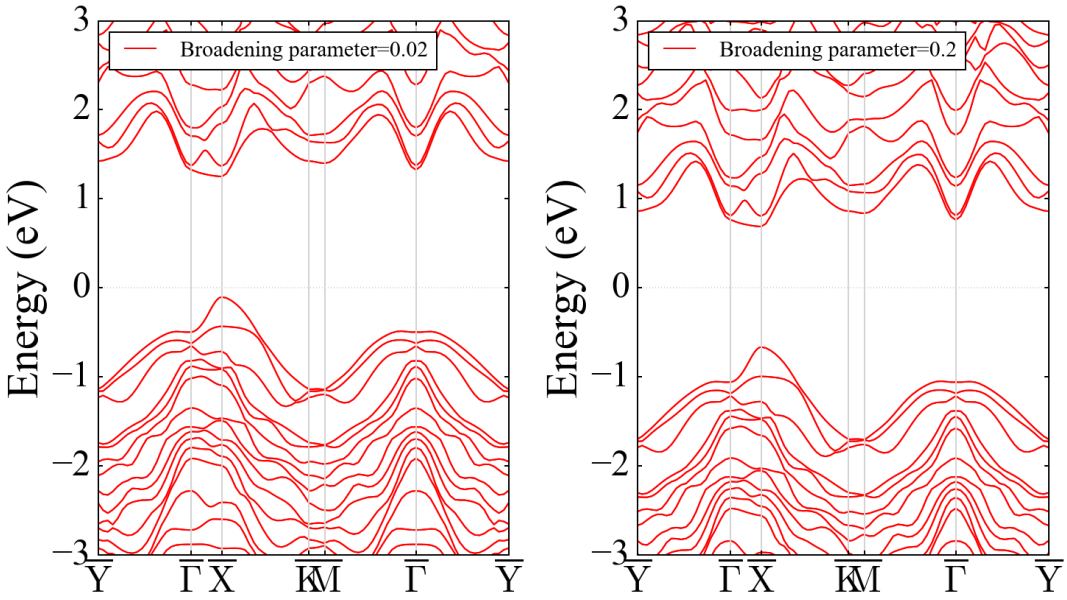
7. Has the structure and stoichiometry of the source material been confirmed using any other methods, e.g. XRD?

A7. We thank our referee for paying attention to the fundamental characterizations regarding the source material which will definitely help us improve the solidity of our results. One of the XRD results can be found in Supplementary Figure 1 of our earlier work [Nat. Commun. 10, 2302 (2019)], which we also quote in below, the inset shows the optical image of GaTe crystal.



8. What is the energy reference of the band calculations, i. e. why is the Fermi level not at the VBM or mid-point of the energy gap? Is there a band going to higher energy at a momentum not included in the displayed path?

A8. Thanks for the comments. Theoretically, the Fermi level lies in the highest occupied Kohn-Sham state. In the practice, the occupied states are obtained by using a smooth function rather than step function for faster convergence speed. Therefore, the Fermi level of the system is related to the state eigenvalues, smearing methods and broadening parameter. In our first-principles calculations, we use Gaussian smearing and the broadening parameter is set to 0.02. Taking the band structure of monolayer GaTe as an example, when the broadening parameter is increased to 0.2, the Fermi level shifts to the middle of the energy band gap, while the band structure is as the same as that with broadening parameter of 0.02, as shown in figures below. These band structures are consistent with previous theoretical result [Nat. Commun. 10, 2302 (2019)], suggesting the VBM is included in the displayed path.



9. Fig. 1b - it is difficult to see where the bulk symmetry points are. A guiding line connecting the points in 3D would be very helpful.

A9. Thank you for your suggestion. The path connecting the high symmetry points of bulk BZ is plotted in the revised manuscript.

10. Fig. 1h has dots between G-Y and lines between G-X. It is easy to see the color of the lines along G-X, but very hard to follow these along G-Y.

A10. Thank you for your suggestion. The band structure has been plotted by the lines in the revised manuscript.

11. Fig. 2 - is this really a binding energy scale? It looks like a kinetic energy scale.

A11. We thank our referee for finding out this typo, although this part has been removed from our revised manuscript.

12. In the discussion, the authors state that the anisotropy is the result of a strong bulk-surface interaction. This is misleading, since the anisotropy of the system is already established by the crystal structure. It may be more correct to say that the anisotropy is modified by the dimensionality of the system.

A12. Thanks for the comments. It is generally known that the in-plane

anisotropy of electronic structures originates from the low crystallographic symmetry [Nat. Rev. Phys. 1, 306-317 (2019)]. Within this scenario, the in-plane anisotropy of hole effective mass of monolayer GaTe should be consistent with the one that extracted from the APRES spectra of GaTe bulk. However, our first-principles calculations reveal the energy band dispersion of monolayer GaTe is inconsistent with the ARPES spectra, indicating the in-plane anisotropy of band structure of GaTe is not dominated by the reduced crystalline symmetry. Moreover, the band structure of infinitely extended bulk model also could not be used to interpret the observed anisotropic band structure of GaTe. These results suggest that the bulk-surface interaction in bulk with finite size might play an important role in the anisotropic electronic structure of GaTe. We then perform the band structure calculation of a slab configuration with thickness of 7-layer GaTe which includes the bulk-surface interaction. It is found that the in-plane anisotropic band structure of slab model is consistent with our ARPES spectra. Further analysis indicates the anisotropic band structure is not a result of quantum confinement effect, as shown in Fig.S3 in the supplementary materials. Therefore, the observed anisotropy of electronic energy bands originates from the strong bulk-surface interaction.

Reviewer #3:

In this manuscript, the authors report ARPES and first-principles band structure calculation studies of GaTe. By using ARPES, they have found strong anisotropy in the effective mass of valence-band dispersion, and concluded the importance of bulk-surface interaction to explain the contradicting ARPES data and band calculation. Although this work may be useful for understanding the evolution of overall band structure on GaTe from the bulk to the monolayer limit, I do not find any new physics and significance of the present study. Therefore, I do not recommend the publication of this manuscript in Communications Physics. This manuscript may be suitable for publication in more specialized journal. My specific comments are the following.

1) Observation of anisotropic band structure is not at all surprising, because it should be generally realized in many other systems. I do not understand why the authors put this anisotropy as a main issue of the present study.

A1. Thanks for the comments. Conventionally, the in-plane anisotropy of band structure is determined by the reduced crystalline symmetry and thus exhibits layer-independent feature in the anisotropic layered materials [Nat. Rev. Phys. 1, 306-317 (2019)]. Our work shows the anisotropy of highest valence band of monolayer GaTe is inconsistent with that of GaTe bulk obtained by ARPES, and the band structure of infinitely extended bulk model of GaTe also doesn't agree with the experimental result. These suggest the observed in-plane anisotropy of band structure of GaTe doesn't originate from the low crystalline symmetry. Further analysis indicates the observed in-plane anisotropic band structure of GaTe is dominated by bulk-surface interaction.

In addition, our theoretical studies show that a direct-to-indirect-to-direct band gap transition could be found as the number of layers increases from monolayer to few-layer GaTe, and the anisotropy of hole effective mass shows layer-dependent character. Moreover, the polarized Raman spectra of GaTe thin films shows strong in-plane anisotropy of the Raman intensity which is consistent with that of bulk GaTe. The corresponding results are shown in Fig.S11 and Fig.S12 in the supplementary materials. This indicates the few-layer GaTe maintains monoclinic phase and the anisotropic band structure evolution with thickness for GaTe is feasible.

2) The meaning of "bulk-surface interaction" is unclear. Such interaction would be limited to a very thin region (at most a few nm) and it would not play a role to control bulk-originated physical properties. If the authors want to say that it affects the band structure for a thin samples, they should show such an experimental evidence.

A2. We thank our referee for pointing out this important issue which makes the topic of our manuscript become clear. In this work, the in-plane anisotropic

valence bands of GaTe obtained by ARPES couldn't be interpreted by the band structure of infinitely extended bulk model, which works for the case of black phosphorus [Nat. Nanotechnol. 9, 372-377 (2014)]. Moreover, the anisotropy of hole effective mass of monolayer GaTe also is inconsistent with experimental result. This is different with the conventional realization that the in-plane anisotropy of band structure in many anisotropic layered materials is determined by the reduced in-plane crystalline symmetry and thus exhibits layer-independent character [Nat. Rev. Phys. 1, 306-317 (2019)]. Considering the fact that the monolayer and infinitely extended bulk model neglect the bulk and surface effect, respectively. We then perform the band structure calculation of 7-layer GaTe slab configuration which includes bulk-surface interaction naturally. The in-plane anisotropic band structure of 7-layer slab model is in agreement with that obtained by ARPES. Furthermore, we find that the in-plane lattice constant and band gap of 30-layer GaTe is very close to those of infinitely extended bulk model, while the anisotropy of hole effective mass of both systems is opposite. These results indicate the observed in-plane anisotropy of band structure of GaTe is dominated by the bulk-surface interaction rather than the quantum confinement effect. Since the surface of a solid is a simple type of interface, the bulk-surface interaction is considered as a result of the interface effect.

In our submitted manuscript, the statements about the influence of bulk-surface interaction on the few-layer GaTe are misleading, since the band structure of 3-layer GaTe is inconsistent with our ARPES spectra. We have removed such statement from the revised manuscript.

3) If the authors wish to discuss the bulk-surface interaction, they need to experimentally distinguish the bulk and surface bands by performing the photon-energy-dependent ARPES experiments. Without the experimental identification of the bulk and surface bands and more sophisticated comparison between the experimental and calculated band structures, it would be difficult to

discuss the nature of bulk-surface interaction.

A3. Motivated by our referee, we conducted more ARPES experiments on synchrotron specifically focused on photon energy-dependent (k_z) and polarization-dependent measurements. The photon energy-dependent ARPES measurements were carried out using photons ranging from 11 to 23 eV due to the limitation of the instruments, while this photon energy range is complementary to the earlier experiments [Phys. Rev. B 65, 115201 (2002)]. The ARPES intensity near E_F as a function of the momentum k_y as well as the probing photon energy is shown in Fig.S5 in the supplementary materials. The cross-section of the Fermi surface seems to be rather slender along the k_z direction, suggesting that the k_z dispersion is considerably weak. It is worthy to note that the measured k_z dispersion is less strong than expected from the calculations, which is consistent with the results reported before [Phys. Rev. B 65, 115201 (2002)]. Furthermore, no obvious surface states have been observed in our experiments and nor in the earlier measurements [Phys. Rev. B 65, 115201 (2002)], the absence of dangling bonds at the GaTe surface shall play an important role in preventing the surface states from emerging.

Fig. 2(g) in the revised manuscript shows the scheme of our polarization-dependent measurements. The selection rule indicates that the p(LH) polarization should be sensitive to probe the p_z and p_x orbitals, while for the s(LV) polarization, the transition matrix element is detectable only for photoemission originating from p_y orbital. According to our theoretical calculations based on the 7-layer slab model that shown in Fig. 2(f), the VB top is dominated by the p_z orbital. Here, as we can see in Fig. 2(h), our measurements using p(LH)-polarized light yield stronger spectral weight for the VB top than using s(LV) polarization, moreover, the VB locates between -1.5 and -2 eV below E_F that also dominated by the p_z orbital is significantly more distinguishable when probing with p(LH)-polarization. As for VB surrounding the Γ point while locates at -1.0 eV and higher binding energies is dominated by p_x and p_y orbitals,

these band features are both pronounced under different polarizations. The distinguishing spectral weight distributions between the two measurements illustrate that the VB top host a predominantly different orbital makeup compare to band structures reside at binding energies higher than -1.0 eV.

Besides the aforementioned ARPES results, we fabricated a series of h-BN encapsulated GaTe thin flakes with different layer thickness and performed polarized Raman spectroscopy, here, the 3.53 and 4.87 nm GaTe thin flakes were identified by Raman mapping method that they both have close binding and thus the same in-plane orientation with the much thicker bulk part, respectively. The corresponding results are shown in Fig.S11 and Fig.S12 in the supplementary materials, in contrast to the early reported results that a monoclinic to hexagonal phase transition happens with the decreasing of the GaTe layer thickness [Small 17, 2007909 (2021), Phys. Chem. Chem. Phys. 18, 18719-18726 (2016).], our results demonstrate that the GaTe monoclinic phase is robust for the flake thickness down to 3.5 nm, this suggests the GaTe thin flake may be very sensitive to ambient conditions, while our calculations based on few layer GaTe slab model is quite rational.

4) ARPES data for the K-deposited samples tell us nothing. To show expected band shift due to the surface electron doping or surface band bending adds no new insights into the electronic states of GaTe.

A4. We agree with our referee on this point that the discussion of potassium doping to manipulate GaTe surface is straying from the main theme of this paper to a certain degree, we decided to remove this part and put in some more experimental results that of relevance, eg., photon energy-dependent and polarization-dependent ARPES measurements as well as layer-dependent Raman spectroscopy as presented before.

5) Although the authors have calculated layer-dependent band structure and suggested the direct-indirect-direct transition, this transition is not supported by the

experiment. Again, ARPES experiments for monolayer and a few layer GaTe samples would be necessary.

A5. We partly agree with our referee on this point. Obviously, this is also related to the photoelectron mean free path which is unknown in GaTe a priori, to be precise, but it is presumably less than 1 nm if one takes the aforementioned photon energy range into account [Surf. Interface Anal. 1, 2 (1979)] which means the effective photoelectron signal comes from the very top layers of GaTe surface. However, this doesn't necessarily mean that the ARPES results we got solely represent the surface or the bulk, instead, our theoretical slab model shows the best agreement with the experimental results. This is the point that we run the story here.

Certainly, some few-layer samples would be relatively more realistic, there is also no doubt that the project will face more challenges over the course of the ARPES experiments, ie., some micro-ARPES even nano-ARPES equipment is needed which is beyond the reach of us at the present pandemic situation. In order to circumvent this dilemma, we fabricated a series of h-BN encapsulated GaTe thin flakes with different layer thickness and performed polarized Raman spectroscopy, the results are discussed in part 3 which indicates our calculations based on few-layer GaTe is rational, although future experiments like photoluminescence and even nano-ARPES will be important to verify our theoretical predictions.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript "Strong bulk-surface interaction dominated in plane anisotropy of electronic structure in GaTe" by Lai et al. has definitely improved since the last time and it is clear that the authors have truly put serious efforts in addressing the criticisms previously made.

In particular, the discussion about the crucial differences between single layer and bulk GaTe is now very clear and even reasonable given the strong motivation given by the authors. The new discussion of the main manuscript for the reasons behind the anisotropy is now straightforward and really well presented. The referee has appreciated the way the message is now given.

Matrix elements have been properly addressed. The only thing, but it is of minor nature, which in my opinion is misleading is the use of "discrete feature along GY". I would rather suggest the use of "elongated feature" or something similar, because discrete might be confusing for the semiconductor community (discrete in energy like quantum well, k-quantization etc..).

Based on the excellent work done by the author I recommend this manuscript for publication.

Reviewer #2 (Remarks to the Author):

The resubmitted manuscript by Lai and co-workers has been substantially revised in an effort to both improve the clarity of the language and to strengthen the authors' arguments. In particular, the authors have removed reference to experiments and calculations involving doping with potassium, and have added new data including polarization and photon energy dependent ARPES as well as Raman measurements. While I find the readability of the revised manuscript has been improved by these revisions, there are a number of major issues remaining with the analysis and interpretation. Specifically, the authors fail to account for the out-of-plane momentum in the ARPES experiment, and since most of their conclusions are built on the effective mass extracted from this data (which is not likely to be at a suitable kz), I do not believe the authors' interpretation and conclusions are supported by their data. I do not recommend publication of the manuscript in its current form; in my opinion, major revisions in both analysis and interpretation are required.

The authors' responses to the previous referee reports are mixed. While the authors have clearly made an effort to address the referees' comments, their responses contain the same major concerns outlined below. I note that these concerns have only been possible to judge now that the authors have provided sufficient information on their crystals and ARPES experiments, which should have been included in the original manuscript submission.

1. Experimentally, the authors study bulk GaTe. The fact they are using a surface sensitive probe does not invite comparison with theoretical calculations of few-layer GaTe. For example, comparison of bulk ARPES data with calculations

of the monolayer is not meaningful, and may even be misleading. The slab geometries may approach a meaningful comparison for thick slabs, but the out-of-plane momentum of the experiment must be accounted for (see below). I do not agree with the authors' interpretation of the outermost layer of their slabs as the surface and all other layers as bulk. This can be seen from the authors' own data: based on Fig. 2e, the topmost band at Gamma and X is a "bulk" band, and yet this clearly shows a strong dependence on the number of layers, e.g. Fig. 3j.

2. The authors take no account of the out-of-plane momentum in the analysis. They only compare the extracted effective masses with the LZH plane of the bulk calculation. In reality, for a bulk crystal measured by ARPES, the out-of-plane momentum could be anywhere in the Brillouin zone depending on the inner potential of the material. The photon energy dependent measurements (Fig. S5) imply there is some dispersion in kz (as expected for a bulk system). The authors make no effort to interpret this properly. This is a missed opportunity to check the dispersion (and therefore effective masses) at a photon energy that corresponds to the VBM. Since there is large dispersion between Gamma and Z in the bulk system, even a small offset in kz from the VBM could lead to large discrepancies in the extracted effective mass.

3. I also have doubts about the reliability of the extracted effective masses, irrespective of whether kz is properly accounted for. These form the basis for the subsequent conclusions by the authors. However, the top of the valence band is very weak in the ARPES data (Fig. 1c), and I struggle to see the dispersion upon which this is based. The authors overlay their "fits" to the data in Fig. S1, but it is not clear how these have been determined. For example, only three data points are indicated along kx. Given the weak intensity from this band, I expect there are large errors in estimating its mass.

4. On a number of occasions, the authors refer to a Fermi surface. Their material is an insulator - there is no Fermi surface.

Reviewer #3 (Remarks to the Author):

At first, I appreciate the authors for their effort to revise the manuscript according to the suggestions from the reviewers. I found that the revised manuscript becomes more accessible to the readers. In particular, I could follow the logic of the manuscript more easily. I have some additional comments on the revised manuscript which needs to be addressed before I recommend the publication of this manuscript in Communications Physics.

1) Authors emphasize the importance of "bulk-surface interaction" based on the fact that the ARPES data do not agree with the DFT calculation for "surface-representative" monolayer as well as "bulk-representative" bulk crystal, but rather agree with that for 7ML. While the authors suggest that the calculation for 7ML naturally includes the "bulk-surface interaction", I still do not feel comfortable to say "bulk-surface interaction", because its definition is still vague. What is the exact physical

meaning of the "bulk-surface interaction"? Interaction of surface state with the bulk state despite the fact that the surface state is absent? If the surface state is absent in this system, could it be still explained within the framework of quantum confinement? Did the authors consider a possibility that the band structure observed by ARPES is different from the genuine bulk states of GaTe because of the surface effect?

2) The authors claim that the ARPES data for bulk GaTe cannot be reproduced by the bulk band calculation regarding the in-plane anisotropy, and the bulk band calculation is not a good starting point to correctly interpret the experimental data. Based on this basic disagreement, it would be questionable to experimentally realize the direct-indirect-direct transition that is concluded purely form the slab calculations. In other words, I don't know to what extent one can reply on the discussion of the slab calculations which do not agree with the experimental data.

3) To show the absence of kz dispersion, it is insufficient to just show photon-energy dependence of the ARPES intensity at EF, especially for the insulating material which in principle has not states at EF. Authors should show experimental band dispersion (ARPES intensity) at each photon energy.

Editorial Office

Communications Physics

February 23, 2022

Response to comments on Manuscript: *Strong bulk-surface interaction dominated in-plane anisotropy of electronic structure in GaTe*

Dear Editor,

We are very grateful for the fruitful peer reviews of our manuscript by editors and all referees, which significantly improves the quality of our work. Following the suggestions of the reviewers, we revised the manuscript carefully and carried out point-by-point response to the referees' comments. The main revisions of the manuscript are summarized here:

1. To measure the energy band dispersion along the out-of-plane (k_z) direction, we extended the probing photon energy to 34 eV which approaches the upper limit of the beamline. In our revised manuscript, the photon energy-dependent ARPES measurements were carried out using photons ranging from 11 eV to 34 eV. This larger energy range almost covers one Brillouin zone along the k_z direction, which can provide more comprehensive information about the energy band dispersion of GaTe.

2. A detailed discussion about the physical meaning of the bulk-surface interaction has also been given in the revised manuscript.

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The manuscript "Strong bulk-surface interaction dominated in plane anisotropy of electronic structure in GaTe" by Lai et al. has definitely improved since the last time and it is clear that the authors have truly put serious efforts in addressing the criticisms previously made.

In particular, the discussion about the crucial differences between single layer and bulk GaTe is now very clear and even reasonable given the strong motivation given by the authors. The new discussion of the main manuscript for the reasons behind the anisotropy is now straightforward and really well presented. The referee has appreciated the way the message is now given.

Matrix elements have been properly addressed. *The only thing, but it is of minor nature, which in my opinion is misleading is the use of "discrete feature along GY". I would rather suggest the use of "elongated feature" or something similar, because discrete might be confusing for the semiconductor community (discrete in energy like quantum well, k-quantization etc..).*

Based on the excellent work done by the author I recommend this manuscript for publication.

Answer 1.

We greatly appreciate the referee for recommending our work for publication. Again, we thank the referee for all the fruitful suggestions that help improving our understanding of the electronic properties of GaTe. In the revised manuscript page 5, we have removed the misleading word "discrete" and revised the sentence as "The valence band spectral intensity along $\bar{\Gamma}$-$\bar{X}$ direction is elongated, which implies a stronger dispersion of the highest valence band along y direction than that along x direction."

Reviewer #2 (Remarks to the Author):

The resubmitted manuscript by Lai and co-workers has been substantially revised in an effort to both improve the clarity of the language and to strengthen the authors' arguments. In particular, the authors have removed reference to experiments and calculations involving doping with potassium, and have added new data including polarization and photon energy dependent ARPES as well as Raman measurements. While I find the readability of the revised manuscript has been improved by these

revisions, there are a number of major issues remaining with the analysis and interpretation. Specifically, the authors fail to account for the out-of-plane momentum in the ARPES experiment, and since most of their conclusions are built on the effective mass extracted from this data (which is not likely to be at a suitable kz), I do not believe the authors' interpretation and conclusions are supported by their data. I do not recommend publication of the manuscript in its current form; in my opinion, major revisions in both analysis and interpretation are required.

The authors' responses to the previous referee reports are mixed. While the authors have clearly made an effort to address the referees' comments, their responses contain the same major concerns outlined below. I note that these concerns have only been possible to judge now that the authors have provided sufficient information on their crystals and ARPES experiments, which should have been included in the original manuscript submission.

1. Experimentally, the authors study bulk GaTe. The fact they are using a surface sensitive probe does not invite comparison with theoretical calculations of few-layer GaTe. For example, comparison of bulk ARPES data with calculations of the monolayer is not meaningful, and may even be misleading. The slab geometries may approach a meaningful comparison for thick slabs, but the out-of-plane momentum of the experiment must be accounted for (see below). I do not agree with the authors' interpretation of the outermost layer of their slabs as the surface and all other layers as bulk. This can be seen from the authors' own data: based on Fig. 2e, the topmost band at Gamma and X is a "bulk" band, and yet this clearly shows a strong dependence on the number of layers, e.g.Fig. 3j.

A1. We thank our referee for reviewing our work in a symbiotic way about the experiment and theoretical model which is helpful. Generally speaking, the in-plane anisotropy of band structure often originates from the low crystallographic symmetry in many anisotropic layered semiconductors. This means the in-plane anisotropy of hole effective mass evolves in a way which is independent of the layer thickness [Nat. Rev. Phys. 1, 306-317 (2019)] i.e., the in-plane anisotropy of hole effective mass for monolayer would be the same as

that of the bulk system. Thus, from our point of view, it is necessary and reasonable to find a suitable theoretical model to interpret the ARPES spectra gained from GaTe bulk crystals, especially, when the infinitely extended bulk model contradicts the ARPES results and we do not know the electron inelastic mean free path in GaTe a priori. Besides, the data we supplemented at the end of last year shows that the k_z dispersion is rather weak (see below) which is also against the bulk model calculations.

Exactly as our referee pointed out, the topmost valence band in GaTe presents layer-dependent feature as the number of layers increases from 1 ML to 5 ML. Here, the key to interpret the ARPES spectra using a slab model is to find out the reasonable thickness of such a slab. As shown in Fig.S3b in the supplemental information, as well as in Fig.3e-j in the revised manuscript, the position of VBM and the anisotropy of hole effective mass for multilayer GaTe are consistent with the ARPES results when the thickness increase from 5 ML to 30 ML. These layer-independent results indicate the calculated band structure from 7 ML slab model could be used to interpret the ARPES spectra, and the way we distinguish the surface and bulk region in the 7 ML slab model is reliable. This is also the method one uses in studying other layered materials, such as $MoTe_2$[Phys. Rev. Lett. 126, 106602 (2021)].

We would like to mention again our polarized Raman spectroscopy results from a series of h-BN encapsulated GaTe thin flakes with different layer thickness. The corresponding results are shown in Fig.S13 and Fig.S14 in the revised supplementary information, in contrast to the early reported results that a monoclinic to hexagonal phase transition happens with the decreasing of the GaTe layer thickness [Small 17, 2007909 (2021), Phys. Chem. Chem. Phys. 18, 18719-18726 (2016).], our results demonstrate that the GaTe monoclinic phase is robust for the flake thickness down to 3.5 nm, this suggests the GaTe thin flake may be very sensitive to ambient conditions, while our calculations based on few

layer GaTe slab model is quite rational.

2. The authors take no account of the out-of-plane momentum in the analysis. They only compare the extracted effective masses with the LZH plane of the bulk calculation. In reality, for a bulk crystal measured by ARPES, the out-of-plane momentum could be anywhere in the Brillouin zone depending on the inner potential of the material. The photon energy dependent measurements (Fig. S5) imply there is some dispersion in kz (as expected for a bulk system). The authors make no effort to interpret this properly. This is a missed opportunity to check the dispersion (and therefore effective masses) at a photon energy that corresponds to the VBM. Since there is large dispersion between Gamma and Z in the bulk system, even a small offset in kz from the VBM could lead to large discrepancies in the extracted effective mass.

A2. We thank our referee for pointing out the out-of-plane momentum issue. We fully agree with our referee on the statement of a precise ARPES experiment, which is especially reasonable when one deals with band structure of strong k_z dependence. As GaTe is a layered two-dimensional material, its k_z dependence is actually weak to some degree. During the first round of the reviewing process, we included the photon energy-dependent measurements that carried out using photons ranging from 11 to 23 eV. Here, we further extended the probing photon energy to 34 eV which almost hits the limit of the beamline (the flux is relatively low), consequently, the whole photon energy range (11 to 34 eV) can almost cover one Brillouin zone along the k_z direction. As shown in Fig.S5 in the revised supplementary information, the ARPES intensities around E_F as a function of the momentum k_y as well as the probing photon energy are rather slender (i.e. along the k_z direction), suggesting that the k_z dispersion is considerably weak. From the weak dispersions, photon energies 20 eV and 30 eV seem to be corresponding to high-symmetry points. After considering the k_z momentum value, an inner potential V_0 of 16.4 eV has been obtained which qualitatively agrees with the earlier experiments [Phys. Rev. B 65, 115201 (2002)]. In contrast to the bulk model calculations where the band structures at Γ and Z points have

obvious differences, the VB top at the two different high-symmetry points are quite close and their dispersions are similar as shown in Fig.S6 in the revised supplemental information, we conclude that the influence of k_z is minor in GaTe. Here we emphasize again that the measured k_z dispersion is less strong than expected from the calculations based on bulk model, which is also consistent with the results reported before [Phys. Rev. B 65, 115201 (2002)].

3. I also have doubts about the reliability of the extracted effective masses, irrespective of whether kz is properly accounted for. These form the basis for the subsequent conclusions by the authors. However, the top of the valence band is very weak in the ARPES data (Fig. 1c), and I struggle to see the dispersion upon which this is based. The authors overlay their "fits" to the data in Fig. S1, but it is not clear how these have been determined. For example, only three data points are indicated along kx. Given the weak intensity from this band, I expect there are large errors in estimating its mass.

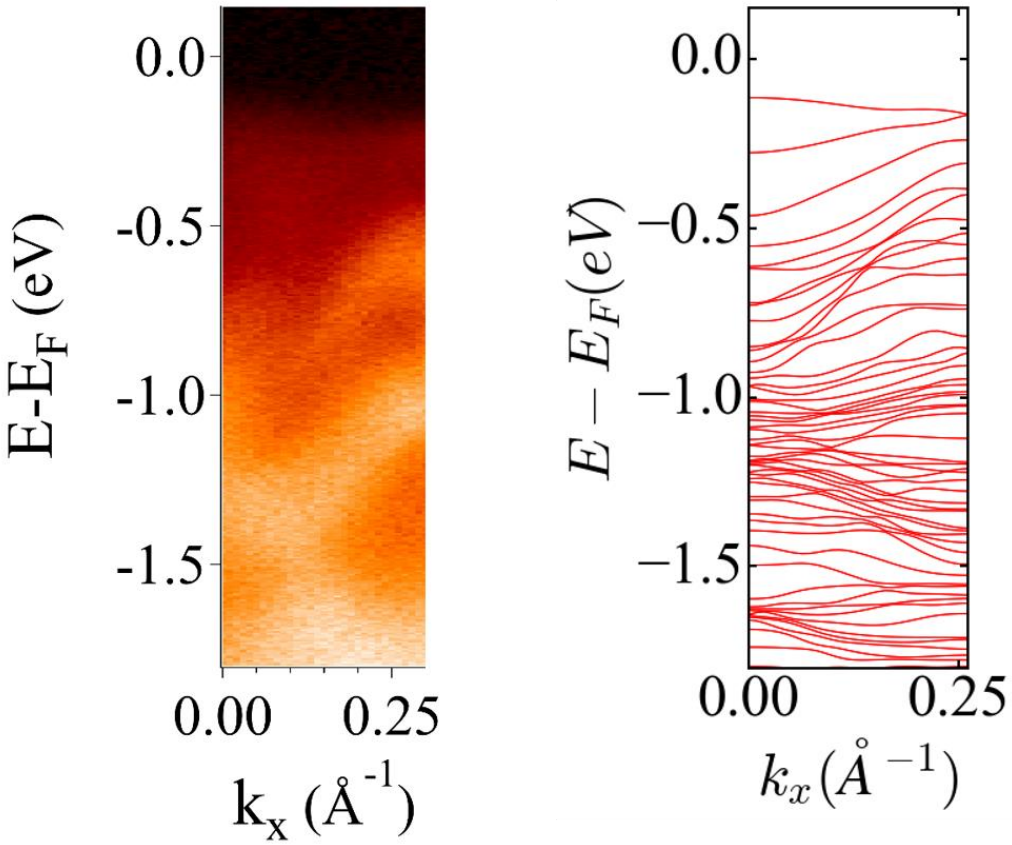
A3. We thank our referee for looking into the dispersions along k_x direction. Here we attached a figure in which the mentioned dispersions are 'magnified' so that this should offer better visualization. Just like the dispersions along k_y direction, the bands near E_F along k_x direction are also very weak, however, from the attached figure, we can see that the trends of the band dispersion are consistent with our slab model calculations. We have tried on both synchrotron and helium lamp for some time, there are several reasons preventing us from having a fine resolution:

i) The VB top along k_x direction is dominated by p_z orbital, same as the VB top along k_y direction, as have being discussed in the polarization-dependent ARPES results, the p_z orbital can only be partially detected on the synchrotron which results in poor resolution. The data shown in Fig. 1c as well as the figure attached here were collected by a helium lamp (21.2 eV), although there is no polarization dependence, the spectra intensity is still low.

ii) The momentum periodicity along the k_x direction is ~0.25 1/Å, which is only

one third compare with the k_y direction due to the nature of low-crystalline symmetry.

iii) The sample can only be measured in liquid nitrogen or higher temperature range, otherwise, the sample will become hardly conductive.



'Magnified' band dispersions along k_x direction from experiment and slab model calculations.

4. On a number of occasions, the authors refer to a Fermi surface. Their material is an insulator - there is no Fermi surface.

A4. We thank our referee for the comments. This misleading statement has been removed from the revised manuscript.

Reviewer #3 (Remarks to the Author):

At first, I appreciate the authors for their effort to revise the manuscript according to the suggestions from the reviewers. I found that the revised manuscript becomes more accessible to the readers. In particular, I could follow the logic of the manuscript more easily. I have some additional comments on the revised manuscript which needs to be addressed before I recommend the publication of this manuscript in Communications Physics.

1) Authors emphasize the importance of "bulk-surface interaction" based on the fact that the ARPES data do not agree with the DFT calculation for "surface-representative" monolayer as well as "bulk-representative" bulk crystal, but rather agree with that for 7ML. While the authors suggest that the calculation for 7ML naturally includes the "bulk-surface interaction", I still do not feel comfortable to say "bulk-surface interaction", because its definition is still vague. What is the exact physical meaning of the "bulk-surface interaction"? Interaction of surface state with the bulk state despite the fact that the surface state is absent? If the surface state is absent in this system, could it be still explained within the framework of quantum confinement? Did the authors consider a possibility that the band structure observed by ARPES is different from the genuine bulk states of GaTe because of the surface effect?

A1. Our heartfelt thanks to our referee for pushing and helping us make the concept clear.

As shown Fig.S3a in the revised supplemental information, the values of the in-plane lattice constant and band gap of multilayer GaTe gradually converge and are close to those of bulk model when the number of layers increases to 30 ML. The anisotropy of hole effective mass of 8 ML GaTe is consistent with that of 30 ML GaTe. These results indicate that the quantum confinement effect doesn’t play a primarily role in the in-plane anisotropy of band structure of GaTe. Exactly as the reviewer mentioned, the difference between the anisotropy of topmost valence band of 7 ML slab model and infinitely extended bulk suggests the surface has profound impact on the anisotropy of hole effective masse in

GaTe. However, this does not mean that the measured in-plane anisotropy in GaTe is determined only by the surface. Notice that with the number of layers decreasing to monolayer, a higher and higher specific surface area will be expected in the system compare with the bulk counterpart and in turn, we assume that the surface effect will dominate the band structure. As shown in the Fig.2a and c in the revised manuscript, the in-plane anisotropic band structure of monolayer GaTe is inconsistent with our experimental observation. This indicates the surface effect alone wouldn't determine the observed in-plane anisotropy of band structure in GaTe.

Thus, we think that the experimentally measured in-plane anisotropy of energy bands in GaTe doesn't originate from the low-crystalline symmetry and the quantum confinement, while also could not be reproduced by system solely involving surface or bulk effect. Only by considering both the bulk and surface effect does the calculated anisotropic band structure agree with the experimental observations. Hence, there exists a strong bulk-surface interaction which dominates the in-plane electronic structure anisotropy in GaTe.

The bulk-surface interaction originates from the interlayer coupling and out-of-plane periodicity breaking in GaTe. The influence of bulk on the surface is attributed to the interlayer coupling. As shown in the Fig.S7 in the revised supplemental information, after weakening the interlayer coupling of 7 ML GaTe by increasing the interlayer distance of the bulk region, the band structure of the system exhibits an indirect band gap. The VBM of the system is located at the point closed to $\bar{X}$, and contributed by both the p_z and p_{xy} orbitals, rather than the p_z orbitals solely. This feature is close to that of 1 ML GaTe where the VBM is dominated by the p_{xy} orbitals. These results indicates that the interlayer coupling will reduce the surface effect in the multilayer GaTe, which is naturally included in the bulk system. However, even though the number of layers reaches 30 ML, the significant influence of the surface effect on the in-plane band structure

anisotropy in GaTe remains in place. As shown in Fig. S3b in the revised supplemental information, with the number of layers increasing from 8 ML to 30 ML, the hole effective mass along y direction gradually converges to that of bulk model, and a large difference between the hole effective mass of 30 ML and bulk GaTe could still be found for the x direction. As a result, 30 ML GaTe has an opposite in-plane anisotropy compared with that of the bulk model. This means that once the periodicity perpendicular to the cleavage plane of bulk GaTe being broken down, the highest valence band dispersion along x direction becomes much weaker than that along y direction.

As for the possibility that the band structure observed by ARPES is different from the genuine bulk states of GaTe because of the surface effect, if we take the 'universal curve' [Surf. Interface Anal. 1, 2 (1979)] as a reference, the electron inelastic mean free path shall be less than 1 nm, although the exact parameter in GaTe is unknown a priori. Fig.S5 in the revised supplementary information shows that the ARPES intensities around E_F as a function of the momentum k_y as well as the probing photon energy are rather slender along the k_z direction, suggesting that the k_z dispersion is considerably weak, however, we think the surface states is absent from GaTe.

2) The authors claim that the ARPES data for bulk GaTe cannot be reproduced by the bulk band calculation regarding the in-plane anisotropy, and the bulk band calculation is not a good starting point to correctly interpret the experimental data. Based on this basic disagreement, it would be questionable to experimentally realize the direct-indirect-direct transition that is concluded purely form the slab calculations. In other words, I don't know to what extent one can reply on the discussion of the slab calculations which do not agree with the experimental data.

A2. We thank our referee for the comments on both the theoretical and experimental results. The calculated in-plane anisotropic band structure of GaTe bulk is inconsistent with our experimental results. However, this is not the reason

that the direct-indirect-direct transition is not feasible because this transition is obtained based on the band calculations of slab models with different number of layers. The band structures of 5 ML, 6 ML, 7 ML, 8 ML and 9 ML slab models agree with the ARPES results, as shown in Fig.2c, d and Fig.3e-i in the revised manuscript. Therefore, the direct-indirect-direct transition with thickness increasing from 1 ML to 5 ML for GaTe is potentially feasible. Truly, some further and challenging experiments would be necessary. However, we would like to mention again our polarized Raman spectroscopy results from a series of h-BN encapsulated GaTe thin flakes with different layer thickness. The corresponding results are shown in Fig.S13 and Fig.S14 in the revised supplementary information, in contrast to the early reported results that a monoclinic to hexagonal phase transition happens with the decreasing of the GaTe layer thickness [Small 17, 2007909 (2021), Phys. Chem. Chem. Phys. 18, 18719-18726 (2016).], our results demonstrate that the GaTe monoclinic phase is robust for the flake thickness down to 3.5 nm, this suggests the GaTe thin flake may be very sensitive to ambient conditions, while our calculations based on few layer GaTe slab model is quite rational.

3) To show the absence of kz dispersion, it is insufficient to just show photon-energy dependence of the ARPES intensity at E_F, especially for the insulating material which in principle has not states at E_F. Authors should show experimental band dispersion (ARPES intensity) at each photon energy.

A3. We thank our referee for pointing out this k_z issue, which is exactly as the 2nd referee did. During the first round of the reviewing process, we included the photon energy-dependent measurements that carried out using photons ranging from 11 to 23 eV. Here, we further extended the probing photon energy to 34 eV which almost hits the limit of the beamline (the flux is relatively low), while the whole photon energy range (11 to 34 eV) can almost cover one Brillouin zone in the k_z direction. As shown in Fig.S5 in the revised supplementary information, the ARPES intensities around E_F as a function of the momentum k_y as well as the

probing photon energy are rather slender (i.e. along the k_z direction), suggesting that the k_z dispersion is considerably weak. From the weak dispersions, photon energies 20 eV and 30 eV seem to be corresponding to high-symmetry points. After considering the k_z momentum value, an inner potential V0 of 16.4 eV has been obtained which qualitatively agrees with the earlier experiments [Phys. Rev. B 65, 115201 (2002)]. We've also included the band dispersion along k_y direction using different photon energies. In contrast to the bulk model calculations where the band structures at Γ and Z points have obvious differences, the VB top at the two different high-symmetry points are quite close and their dispersions are similar as shown in Fig.S6 in the revised supplemental information.

REVIEWERS' COMMENTS:

Reviewer #3 (Remarks to the Author):

In my opinion, the authors have satisfactorily addressed my remaining concerns regarding the bulk-surface interaction, direct-indirect-direct transition, and kz dispersion. The authors also incorporated my suggestions into the revised manuscript appropriately. I would recommend the publication of this manuscript in Communications Physics in its present form.