Discovery of an unconventional charge modulation on the surface of charge-density-wave material TaTe$_4$
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Abstract

Electronic systems with quasi-one-dimensional (Q1D) Fermi surface tend to form either a charge-density-wave (CDW) or a spin-density-wave ground state at low temperatures due to one-dimensional instabilities. Among various CDW states, surface CDWs are different from that within the bulk due to the reduced dimensionality. Here we report the systematic investigation of charge density modulation on the surface of $\text{in situ}$ cleaved TaTe$_4$ crystal by means of low temperature scanning tunneling microscopy/spectroscopy, corroborated with density functional theory calculation. Well-defined Q1D modulation $\left(4a \times 2a \times 3c\right)$ accompanied with a periodic lattice distortion is clearly observed on the (010) cleaved surface, distinct from that of its bulk CDW $\left(2a \times 2a \times 3c\right)$. Tunneling spectroscopic measurements reveal a partially-opened energy gap about 23 meV around Fermi level. Such gap shows similar spatial variation with the periodicity of surface modulation and diminishes subsequently as temperature rises, which indicates a novel surface-related CDW gap states. The surface modulation vectors fit well with the Fermi surface nesting vectors, derived from the calculated Fermi surfaces. Surprisingly, such surface modulation can be suppressed greatly by applying vertical magnetic field and a critical field about 9.05 T can be estimated from field-dependent data. Our results demonstrate that this unique CDW modulation is strongly related to Fermi surface nesting mediated electron–electron coupling due to the reduced dimensionality of the surface, and can be readily tuned by relatively small magnetic field.

1. Introduction

Charge density wave (CDW) is a periodic modulation of electron density in real space below the critical temperature ($T_{\text{CDW}}$), which opens a gap at the zone boundary of the new unit cell [1]. This charge density modulation changes the potential in the lattice so that the ions move to new equilibrium positions, resulting in a periodic lattice distortion. CDW states are often found to coexist and/or compete with other orders, e.g. the superconductivity in cuprates [2–5] or in transition metal dichalcogenides (TMDs) [6–8]. A variety of underlying mechanisms for CDWs, such as Peierls model [1], electron–phonon coupling [9–11] and electron–electron interactions [12] were proposed to explain the charge density modulation in different
materials, but the origin of various CDW states is still under the debate. Besides, the effects of low dimensionality and interlayer coupling on CDW phases are areas of great interest recently [13–17], which have been demonstrated in mechanical exfoliated ultrathin flakes. Surface CDW could be very different from that in the bulk due to reduced dimensionality [18–20]. For examples, the transition temperature of CDW phase can be enhanced at the surface of some CDW materials [20–23] and also in the monolayer of materials [24–26]. Such enhancement of $T_{\text{CDW}}$ can be attributed to enhanced interactions induced by the decreased dimensionality on surfaces [27, 28]. However, previous measurements of CDW states, e.g. by using transport and transmission electron microscopy, cannot distinguish between the CDWs within the bulk and on the surface, which may experience the difficulties for describing the surface CDW. Although some efforts have been devoted to investigate surface CDWs by surface-sensitive techniques, such as scanning tunneling microscopy (STM) [29, 30], but the study of surface-induced unconventional CDW is still highly demanded.

Quasi-one-dimensional (Q1D) transition metal polychalcogenides TaTe$_4$ and NbTe$_4$ are regarded as CDW materials with presenting commensurate modulations below $T_{\text{CDW}}$, observed by both x-ray and electron diffraction [31, 32]. Though the bulk properties of (Ta, Nb)Te$_4$ have been intensively investigated in the past decades [33–36], however, a systematic study of charge modulation characteristic on the surface of CDW materials is still missing. In this work, we employed low temperature scanning tunneling microscopy/spectroscopy (STM/S) to investigate the surface charge density modulation of TaTe$_4$. STM/S can provide surface structural and local electronic information for surface CDW. A unidirectional charge density modulation with double periodicity of its bulk CDW is observed on the surface of TaTe$_4$. Spectroscopic measurements show a partially-opened gap about 23 meV near the Fermi energy ($E_F$), which varies periodically with surface modulation and diminishes subsequently as temperature rises, strongly suggesting it as a novel surface-related CDW states. The corresponding wave vector of modulation matches well with the Fermi surface (FS) nesting vectors obtained by the first-principle calculations. Moreover, this surface modulation can be suppressed effectively by applying perpendicular magnetic field. Our observations imply that the origin of surface modulation is highly related to the electron–electron (e–e) interaction mediated through Fermi surface nesting, while the reduced dimensionality on the surface enhances the e–e coupling and helps to the formation of surface CDW.

2. Experimental methods

High quality TaTe$_4$ single crystals are grown by chemical vapor transport (CVT) technique in a multi-zone single crystal furnace. Ta and Te powder are mixed at atomic ratio 1:4.3 and sealed with 5–10 mg cm$^{-3}$ iodine in an evacuated quartz tube. The mixture was first heated to 1000 ºC and kept for 12 h. After the required period of heating, sample is slowly cooled down to room temperature. The quartz tube is then placed co-axially in a multi-zone furnace. The reaction zone is kept at 540 ºC and growth zone 440 ºC for 7 days. After slowly cooling down to room temperature, bulk samples with metallic luster are obtained. Samples grown by this method are quite stable in atmosphere. The crystals chosen for STM study were TaTe$_4$ with the size about 2 mm $\times$ 1 mm $\times$ 0.5 mm. Samples were first cleaved in situ at room temperature in ultrahigh vacuum chamber with pressure better than 1 $\times$ 10$^{-10}$ Torr. After the cleavage, the TaTe$_4$ single crystals exhibit a mirror-like surface then were transferred into a cryostat with liquid helium cooling for STM measurements. The STM tip was prepared by chemical etching tungsten wire, following by degassing and electron beam bombardment in vacuum for the cleanliness.

3. Results and discussion

The bulk structure of TaTe$_4$ consists of TaTe$_4$ columns aligned along $c$ axis by forming a tetragonal structure. Each column contains the chains of Ta atoms coordinated by eight Te atoms, Ta atoms are thus in the center of Te square antiprisms. The interchain Te–Te distance is shorter than the intrachain distance, so that Te$_2^{2-}$ dimers are formed between adjacent chains. The shortest Te–Te distance is found between neighboring chains and each Ta atom can be considered as surrounded by eight Te$_2$ dimers. In fact, strong hybridization between the Te$_2$ p$\sigma^*$ orbitals and the Ta d$\sigma$ orbital induces a deep electron pocket [37]. The significant interchain p–d interaction makes TaTe$_4$ much less 1D nature than other polychalcogenides [38]. Bulk TaTe$_4$ is in a distorted CDW phase with a commensurate superstructure ($2a \times 2a \times 3c$) below 475 K [39], which implies a Fermi wave vector $k_F = 1/3c^*$ ($c^*$ is the reciprocal-lattice vector parallel to the chain). Superlattice spots related with three different charge density wave vectors have been observed by electron diffraction [35], i.e. (0, 0, 0), $(a^*/2, a^*/2, c^*)$ and $(a^*/2, 0, c^*)$. As reported previously [40], the Ta–Ta distance is modulated, so that three adjacent Ta ions in a single column displace from the equilibrium...
positions and form the Ta$_3$ trimer for the commensurate phase in the bulk, with a phase difference of $2/3\pi$ between adjacent chains.

TaTe$_4$ crystals can be preferentially cleaved along the ac plane in vacuum and the exposed surface is the (010) surface with Te top terminal layer. Figures 1(a) and (b) show a topographic STM image taken on the TaTe$_4$ surface and a zoomed high resolution image taken at 4.2 K. The large-scaled image reveals a 1D uniform superstructure or modulation nearly covering the area, except for the ends of 1D modulation at defects. Highly-resolved image in figure 1(b) gives not only the atomic structure of TaTe$_4$ (010) surface, but also shows the enlarged unit cell of surface modulated superstructure. Owing to high-resolution capability of STM to reveal surface atomic structure, we can measure surface lattice constants directly from STM images: $a = 6.64$ Å, $c = 6.81$ Å, represented by black rectangle in figure 1(b), which is roughly consistent with the bulk values from previous literature $[31]: a = 6.514$ Å, $c = 6.809$ Å. This also suggests that the cleaving surface is ac plane, similar with NbTe$_4$ material $[41]$. In supplementary materials figure S1 (https://stacks.iop.org/NJP/22/083025/mmedia), we have measured both surface lattice constants $a$ and $c$ over twenty times from images taken from different surface areas, and plot the results in figure S1(b). Obviously, for modulated lattice, the average value of $a$ is 6.65 Å, 2% larger than the bulk value (6.514 Å). The surface lattice constant $c$ is close to the bulk value, which reflects the existence of unidirectional lattice distortion on this surface.

Interestingly, the modulation observed by STM on TaTe$_4$ surface is different from the bulk commensurate modulation of $2a \times 2a \times 3c$. The unit cell of surface modulated superstructure is enlarged to $(4a, 6c)$, indicated by blue rectangle (figure 1(b)). The fast Fourier transformation (FFT) of the STM image (figure 1(c)) shows unambiguously the spots for 1D superstructure/modulation, marked with red dashed circles. According to the registry to the reciprocal lattice vectors $a^*$ and $c^*$, we can assign that the vectors of 1D modulation are $(a^*/4, c^*/6)$ and $(-a^*/4, -c^*/6)$. Another equivalent pair of modulation vectors $[(-a^*/4, c^*/6) and (a^*/4, -c^*/6)]$ are much weaker or missing, which leads to unidirectional 1D nature of surface modulation. We did not observe any signature of Ta$_3$ trimmers on the surface as in the

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**Figure 1.** (a) Topographic image on the surface of TaTe$_4$ with size of $40 \times 40$ nm$^2$, taken at $V_b = -250$ mV and $I_s = 250$ pA and (c) its fast Fourier transformation. Blue and purple dotted circles identify the wave vectors associated with the lattice, red dotted circles in the FFT are the surface modulation wave vectors. (b) A zoom-in STM image with the size of $10 \times 10$ nm$^2$. The averaged unit cell and the enlarged surface unit cell are indicated by the black rectangle and the blue rectangle. (d) and (e) Line cut profiles for two different types of elongated bright spots appearing in (b), indicted by blue and red dashed lines in atomic resolution images, to show the surface corrugation and atomic positions. (f) Proposed schematic structure of the cleaved surface, light blue balls stand for Ta atoms and the green ones are Te atoms. Marked light blue and red ellipses represent two different types of elongated bright spots, marked with the dashed blue and red ovals in (b), respectively.
Figure 2. The evolutions of topographic images and dI/dV spectra with spatial locations and temperatures. (a) Atomically resolved image of TaTe$_4$ surface at 4.7 K, displays clear signs of surface modulation. The $4a \times 6c$ surface unit cell has been marked by blue dotted rectangles. The blue/red ellipses represent for two kinds of elongated bright spots. The imaging conditions for: $V_b = 150$ mV and $I_s = 0.2$ nA with the scan range of $15 \times 15$ nm$^2$. (b) A representative dI/dV spectrum collected at 4.2 K, shows a clear gap feature about $\Delta \sim 23$ meV near Fermi level. Set points: $V_b = 150$ mV, $I_s = 200$ pA and bias modulation for lock-in technique is 9 mV. The gap sizes are determined by measuring the energy separation between the middle points of two gap edges. (c) A series of dI/dV spectra acquired along the blue–green line in (a). The numbers of '1–4' indicate the corresponding dI/dV curves taken on the top of each labeled bright atomic rows, exhibiting the evolution of the gap with spatial locations. The red shaded area highlights electronic DOS suppression around the Fermi level. Here, all spectra were taken at 4.2 K with $V_b = +150$ mV and $I_s = 0.2$ nA. Bias-modulation amplitude was set to 9 mV. (d) Atomically resolved image of TaTe$_4$ surface at 77 K, displays no signs of surface modulation. $V_b = 300$ mV, $I_s = 100$ pA; (e) a representative dI/dV spectrum collected at 77 K, shows no gap feature. Set points: $V_b = -200$ mV, $I_s = 250$ pA and bias modulation for lock-in technique is 8 mV.

bulk. However, from the topographic image, two new elongated bright spots appear alternately along the stripe, indicated by blue and red dashed ovals in figure 1(b). Figures 1(d) and (e) show the atomic structure and their corresponding line profiles of the two new configurations. Each elongated bright spot consists of five Te atoms ($\sim 2c$), which are not on the same line and shows different shapes. The nearest distance between the same type of bright spots is $6c$ along $c$ direction (see figure 1(f)). It is notable that some Te atoms go down due to the lattice distortion [42], which makes them invisible on the STM image. Therefore, an enlarged superstructure ($4a, 6c$) is observed on the surface of TaTe$_4$ (010), distinct from the bulk commensurate modulation ($2a, 2a, 3c$). Novel unidirectional periodic superlattice imply the existence of surface-related modulations. So the studies of the origin and evolution of the observed surface modulation are important.

Structural distortion, charge density modulation or both, are possibly responsible for the observed surface modulation. In order to investigate whether such 1D modulation is structural or electronic phase, e.g. CDW, we provided multiple evidences, including both spectroscopic measurement and local density of states imaging, namely dI/dV mapping. Firstly, charge density wave, as a ground state, which can be stabilized via either e–e interaction or electron–phonon (e–p) coupling or both. This, in turn, results in the formation of energy gap near the $E_F$. Such energy gap tends to decrease with the temperature increasing and finally vanishes as the temperature exceeds to the corresponding $T_{CDW}$. The topographic STM images and differential conductance (dI/dV) curves taken at different temperatures are given in figure 2. Figure 2(a) is an empty-state image of the surface modulation obtained at 4.2 K. Figure 2(b) shows a representative dI/dV spectrum, proportional to the local density of states, taken in the area with 1D modulation at temperature of 4.2 K, which displays asymmetric shape in the bias window. A density of states (DOS) suppression with the energy about 175 meV is firstly observed, smaller than previously reported gap values observed in the TaTe$_4$ bulk ($\sim 0.4$ eV by angle-resolved photoemission spectroscopy, and $\sim 0.37$ eV by optical conductivity...
Figure 3. (a) Topographic image, (b) dI/dV map taken simultaneously and (c), (d) are their corresponding fast Fourier transformation images. Set points: $V_b = -100$ mV, $I_s = 200$ pA and bias modulation for lock-in technique is 4 mV. (e) A zoom-in FFT image of (d). (f) Upper left panel is the bulk Brillouin zone (BZ) of CDW phase, high-symmetry points are indicated. Lower panel is the cross-section of Fermi surfaces along [010] by considering bulk CDW ($2a \times 2a \times 3c$). Four bands cross the $E_F$ of TaTe$_4$ in CDW phase, among which band 1 (blue) and 2 (orange) give rise to open FS while band 3 (brown) and 4 (green) lead to closed Fermi pockets. And upper right panel shows the bands folding of surface ($4a \times 6c$) modulation.

measurement [36]). The ratio of the CDW gap $\Delta$ at $T = 0$ can be estimated by the CDW transition theory which is $2\Delta/k_BT_{\text{CDW}} \approx 3.52$ [43]. Considering that the $T_{\text{CDW}}$ of bulk TaTe$_4$ is about 475 K, the size of bulk CDW gap of TaTe$_4$ in the standard weak coupling theory should be around 72 meV [9]. This large gap is about 2.4 times larger than the CDW prediction. Similar gap energy discrepancy has been observed in other transition metal chalcogenides. A significant large energy gap about 35 meV was observed in traditional CDW material NbSe$_2$ for the corresponding $T_{\text{CDW}} \sim 33$ K [44]. Such discrepancy of gap energy was also reported in IrTe$_2$ surface [45], where a homogeneous full-gap opening of about 0.3 eV was observed over the surface.

Moreover, a smaller but much prominent V-shaped energy gap of $\Delta \sim 23$ meV appears near the $E_F$ inside the large gap. It is worth to note that such tunneling spectrum has been measured many times and the main feature maintains at the different locations that are far from the defects, implying such gap feature is quite universal over the surface. Such small partially-opening gap has not been reported before for this material. In order to study the relationship between this small energy gap and the observed surface 1D modulation, a spectroscopic survey was taken by crossing two surface unit cells, clearly showing the electronic evolution of such energy gap with the modulation. Figure 2(c) shows the dI/dV spectra acquired along a blue–green arrow in figure 2(a), all exhibit similar asymmetric shapes. Beginning from a unidirectional 1D chain labeled by ‘1’, dI/dV spectrum shows firstly a deep gap feature (shading by red color in figure 2(c)) around $E_F$, then gradually develops into a shallow DOS suppression near $E_F$ as located between two 1D chains. Once moving to the top of bright 1D chain, the gap becomes more profound. Such gap-like feature opens periodically at the locations corresponding to ‘bright’ 1D chains. According to our high-resolution STM images and structural analysis, ‘bright’ 1D chain is corresponding to elongated bright spots, which comprise of five surface Te atoms. Clearly, not only the gap size but also the depth of gap varies spatially with surface 1D modulation. The depth variation of gap indeed reflects a reduction in the spectral weight near the Fermi level [46–48]. Thus, the partially-opened gap is closely related with the surface modulation.

Furthermore, as the temperature increases up to 77 K, 1D surface modulation exhibits more disorder (figure 2(d)) and the corresponding gap feature becomes much weaker (figure 2(e)), compared with that at low temperature (4.2 K), suggesting that such gap is closely related to 1D surface modulation and exhibits similar evolution as CDW gap with temperature varying. As discussed above, both spatial and
temperature-dependent spectroscopic results indicate that the 23 meV gap we observed in the present case is a CDW-like gap related with $(4a, 6c)$ surface modulation.

Thus, the appearance of modulation of $(4a, 6c)$ is most likely due to the formation of electronic CDW phase. Usually, both topographic image and electronic local density of states exhibit the same modulation for electronic CDW phase but not the case for the pure structural distortion [49]. In order to discriminate these two aspects, we carried out the differential conductance mapping. Figure 3(a) shows the topographic image taken at $-100$ mV and next to it is the corresponding $dI/dV$ map (figure 3(b)) taken simultaneously by measuring the distribution of local density of states in real space. Figures 3(c) and (d) are the corresponding Fourier decomposition images of the topographic image and the $dI/dV$ map, respectively.

The topographic image in figure 3(a) shows an area which is mostly covered by 1D modulation and presents both atomic resolved features from Te lattice and surface $(4a, 6c)$ superstructure. Small patches of non-modulated area are embedded in between, marked by blue dashed lines. The $dI/dV$ map in figure 3(b) shows similar 1D charge density modulation, matching well with the patterns shown in figure 3(a). The FFT images of the topographic image and the $dI/dV$ map have similar reciprocal lattice vectors and fractional spots, such as $(a'^{*}/4, c'^{*}/6)$ and $(-a'^{*}/4, -c'^{*}/6)$, corresponding to the formation of 1D modulation.

Therefore, the results shown above support that the appearance of surface modulation is attributed to the formation of CDW phase. Besides, the FFT of $dI/dV$ map in figure 3(d), shows much more and stronger fractional spots, which is corresponding to higher harmonic orders of the modulation spots.

By zooming into the center of figure 3(d), a complex scattering pattern appears in the zone center (figure 3(e)). As we know, the CDW state could be induced by e–e interaction through the Fermi surface nesting. On the surface, such e–e interaction can be further enhanced by strong confinement due to the reduced dimensionality. We performed density functional theory (DFT) calculation by using Vienna $ab$ initio simulation package (VASP) [50] within the generalized gradient approximation, parameterized by Perdew, Burke, and Ernzerhof [51]. The band structure corresponding to bulk CDW structure $(2a, 2a, 3c)$ of TaTe$_2$ was calculated and CDW dramatically modified FS of TaTe$_2$ is shown in figure 3(f). Four bands cross the $E_F$ of TaTe$_2$ in CDW phase, among which band 1 (blue) and 2 (orange) give rise to open FS while band 3 (brown) and 4 (green) lead to closed Fermi pockets. By measuring the vectors of $(a'^{*}/4, c'^{*}/6)$ and $(-a'^{*}/4, -c'^{*}/6)$, we found such vectors fit well with the nesting CDW vector $q_{CDW}$ that connects high density nesting points on the Fermi pockets of band 3 (brown). This imply the formation of this CDW phase is highly related with the FS nesting.

It is worth to note that the calculation of FS and first Brillton zone was done by considering bulk CDW structure $(2a, 2a, 3c)$. After considering surface modulation structure $(4a, 6c)$, the bands (figure 3(f)) need to be further folded and produce more Fermi pockets around the central $Γ$ point (upper right panel), which may explain the complex scattering patterns observed in figure 3(e). Another interesting fact is, only one pair of vectors $q_{CDW}$ becomes dominant in the FFT images, that is $(a'^{*}/4, c'^{*}/6)$ and $(-a'^{*}/4, -c'^{*}/6)$, while the intensity of another equivalent vectors pair $[-(a'^{*}/4, c'^{*}/6)$ and $(a'^{*}/4, -c'^{*}/6)]$ is relatively weaker, which produces 1D character of the observed CDW state. To the best of our knowledge, the modifications of phonon dispersion may play a key role in favoring one type of geometry over another [52]. From the surface structure we measured, there exists unidirectional lattice distortion on this surface. As a result, such surface lattice distortion may modify surface phonon modes, which makes the modulation more unidirectional on the surface.

High magnetic fields have proven to be useful to investigate, and even manipulate, CDW states [53]. The Zeeman energy is expected to suppress a CDW state because a CDW couples only bands with the same spin. To explore the magnetic field dependence of this CDW phase, various magnetic fields were applied perpendicular to the sample surface. The insets in figures 4(a)–(d) exhibit $dI/dV$ maps taken at exactly same area under different magnetic fields with same bias ($V_b = -0.1$ V). We perform Fourier analysis on the $dI/dV$ maps in order to quantitively study the evolution of surface CDW with various magnetic fields. Figure 4(e) presents the relative intensity of the surface modulation peaks $(I_{dI/dV})$ in the FFT images, normalized by dividing the intensity of Bragg lattice peaks $(I_{Bragg})$. Such ratio $(I_{dI/dV}/I_{Bragg})$ can be taken as a measurement of the strength of the surface CDW modulation at specified energy. As shown in figure 4(e), the amplitude of $I_{dI/dV}/I_{Bragg}$ decreases with increasing the magnetic field, which implies that CDW state is suppressed by the magnetic field. A linear fit can describe the relationship between the intensity of the surface modulation and the applied field, indicated by the red line in figure 4(e). By extrapolating the linear relation to zero, a critical field about 9.05 T can be obtained for fully suppressing the intensity of surface modulation, leading to $(4a, 6c)$ surface modulation vanished.

The Zeeman energy, $μ_B B/ρ(E_F) B^2$, where $ρ(E_F)$ is the density of states at $E_F$, competes with the CDW condensation energy, $ρ(E_F) Δ(0)^2$. The transition temperature is expected to decrease with increasing field [54], which have been observed in NbSe$_2$ [55]. Above a certain threshold field $Δ(0)/μ_B B$, a uniform CDW is no longer energetically favorable. Consequently, a CDW can be suppressed by high magnetic fields. Similar
Figure 4. The FFT images of the $\frac{dI}{dV}$ maps taken at different magnetic fields. (a) 0 T, (b) 2 T, (c) 4 T and (d) 8 T. Each $\frac{dI}{dV}$ map is shown as an inset, the scale bar is 6 nm. (e) Plot of the intensity of the modulation peaks ($I_{mod}$) in the FFT of the $\frac{dI}{dV}$ maps normalized by the Bragg peak intensity ($I_{Bragg}$) as a function of magnetic field. The red line represents the result of linear fitting. Set point: $V_b = -100$ mV, $I_s = 200$ pA and the magnitude of bias modulation for lock-in technique is 4 mV.

Phenomena have been studied in some quasi-one-dimensional materials, such as organic material (Per)$_2$Au(mnt)$_2$ and oxide Li$_{0.9}$Mo$_6$O$_{17}$ [56–58]. However, the Zeeman energy of 9.05 T is only about 0.524 meV, which is nearly two orders of magnitude smaller than the CDW condensation gap energy 23 meV. Another mechanism instead of Zeeman energy must play an important role for field-induced suppression of surface CDW. Chang et al [53] reported that high magnetic field modifies the coupling between the CuO$_2$ bilayers in the YBCO structure and leads to Fermi surface reconstruction, which also be observed in quantum oscillations of underdoped YBCO with mirror symmetry broken by charge density waves [59, 60]. Since surface CDW we observed is mediated by e–e interaction on the surface, field-modified interlayer coupling can result in Fermi surface reconstruction, therefore greatly suppress the surface CDW. The magnetic field dependence of the surface modulation agrees with the behavior of Q1D surface CDW driven by Fermi surface nesting. Therefore, the magnetic field dependent behavior of CDW, in conjunction with Fourier analysis and the first-principle calculation, indicate that e–e interaction mediated through Fermi surface nesting should be mainly responsible for the formation of CDW phase on the surface of TaTe$_4$.

On the other hand, our experiment shows that the CDW modulation can be detected at bias energies up to $-300$ mV, far exceeding the gap energy (see supplementary materials, figure S2), implies other factor beyond Fermi surface nesting, such as strong coupling-CDW caused by e–p coupling, may play a role in the surface CDW formation of this Q1D system at high energies. For example, in some CDW systems, the local strain can affect the e–p coupling on the surface, which in turn determine the direction of CDW modulation. The similar effect of strain was proposed at the surface of NbSe$_2$ to drive the modulation from tridirectional to unidirectional [61]. It is believed that the $q$-dependent e–p coupling, plays a key role in determining CDW modulation of NbSe$_2$ [62]. Such e–p coupling induced mechanism could also apply to our case for Q1D surface CDW phase of TaTe$_4$. Indeed, differently periodic CDW phase compared with the bulk is reported here, implies the unique nature of the surface situation and will attract special interests to the surface due to the existence of symmetry breaking and may induce novel phenomena. In addition, a nonzero Berry phase suggested in transportation experiments and recent DFT calculation, both imply topological nontrivial properties of this compound [33, 34]. Therefore, further surface-sensitive and topology-related experimental explorations are highly desired in future.
4. Conclusion

In summary, scanning tunneling microscopic/spectroscopic measurements were carried out to investigate the modulation on the surface of the quasi-one-dimensional compound TaTe\textsubscript{4}. The surface modulation was clearly observed and the superstructure of modulated phase is 4$\alpha \times 6c$, which is distinct from its bulk. Spectroscopic measurements show the gap size diminishes as temperature increases. From the first-principle calculations, we found that the wave vector of the surface modulation agrees with the FS nesting wave vector. Furthermore, the electronic surface modulation can be suppressed by applying field. These observations point to the origin of the surface modulation is strongly related to e–e interaction through the FS nesting, while the e–p interaction may play a role in stabilizing the surface CDW formation at high energies. Thus, TaTe\textsubscript{4} provides a new platform for investigating the formation mechanism of surface-related CDW and may shine a light on future study of the relationship between CDW states and topological phases.

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