Doping dependent charge density wave contrast inversion in topographic STM images of TiSe₂

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ABSTRACT

Contrast inversion (CI) between opposite polarity scanning tunneling microscopy (STM) images, although seen as a hallmark of the charge density wave (CDW) ground state, is only rarely observed. Combining density functional theory and STM on pristine 1T-TiSe₂, we show that CI takes place at increasingly negative sample bias as the CDW gap shifts to higher binding energy with electron doping. There is a point where the gap is shifted so far below the Fermi level (E₉) that CI disappears altogether. Contrast inversion thus gives a different insight into the CDW gap, whose measurement by scanning tunneling spectroscopy is notoriously controversial. It provides unique evidence that the CDW gap is not bound to E₉ and that it can develop deep inside the valence band, an explicit constraint on any model description of the CDW phase transition.

The charge density wave (CDW) ground state is an atomic length scale periodic distortion, combining lattice and charge degrees of freedom [1]. The precise mechanism driving this quantum phase transition remains largely unknown. Fermi surface nesting, electron-electron or electron-phonon interactions, and coupling of electrons to other degrees of freedom in the host crystal are among the main mechanisms discussed over the years [2, 3].

Below the CDW phase transition, atoms rearrange into periodic lattice distortions. Concomitantly, charge is redistributed in real space to form alternating regions of charge accumulation and charge depletion. In the classic Peierls mechanism, mostly states in the vicinity of the Fermi level (E₉) are involved in the CDW formation and a gap opens at E₉.

Scanning tunneling microscopy (STM), owing to its high spatial topographic resolution, is an ideal probe to characterize the real space charge ordering. In the Peierls scenario, STM images of the CDW at negative bias will show enhanced intensity over charge accumulation regions, whereas images of the same area at positive bias will show enhanced intensity over charge depleted regions. This is known as contrast inversion (CI) of the CDW STM contrast between positive and negative sample bias images.

Contrast inversion is often considered a hallmark of the CDW contribution to the STM topographic signal. However, clear CI between opposite polarity STM images has only been reported on very few instances [4, 5], including high temperature superconductors [6] and transition metal dichalcogenides (TMDs) [7]. In a thorough theoretical analysis for 2H-NbSe₂, Sacks et al. [8] conclude that CI does not take place in this material due to band structure effects. They further contend that CI is in general not expected for two-dimensional (2D) CDW systems. In a more recent STM study of TaSe₂, TaSe₂ and NbSe₂, Dai et al. [9] conclude that strong lattice distortions completely mask possible CI arising from electronic contributions to the CDW amplitude in the topography.

In addition to the real space reconstruction introduced above, the CDW ground state is also characterized by a gap in the electron density. This gap does in general not open for all momenta. It is therefore challenging to measure accurately by scanning tunneling spectroscopy (STS), which is a momentum averaging technique. Consequently, there is not only a controversy over the magnitude of the CDW gap measured by STS, but also over its location with respect to E₉.

In this study, we achieve novel insights both into the CDW gap and into the contrast inversion in STS and STM experiments. We show that the absence of CI in opposite polarity STM images is a direct consequence of the CDW gap not opening at E₉. When present, CI informs about the CDW gap amplitude, which is often significantly larger than expected from the phase transition temperature. Finally, detailed analysis of CI provides direct clues about the inadequacy of Fermi surface nesting as the main mechanism driving the CDW phase transition.
Simple visual inspection of the constant current STM images presented in Fig. 1 (top row) shows that CDW contrast inversion does not happen between the opposite polarities data, but between the frames acquired at -100 mV and -300 mV. These images acquired at different bias voltages were aligned with atomic scale precision using well-identified single atom oxygen and titanium defects resolved in large-scale images [10]. Contradictory to these experimental findings, detailed DFT calculations for undoped pristine 1T-TiSe₂ predict CDW contrast inversion between -100 mV and +100 mV (Fig. 1, bottom row), similarly to the classic Peierls model.

DFT does reproduce the experimental observation when doping electrons into the unit-cell (Fig. 1, middle row). The energy where Cl takes place in this case depends on carrier concentration, shifting to higher binding energy with increasing electron content (Extended Data Fig. 1). Interestingly, there is a practical limit as to how far Cl can be observed at negative bias. Indeed, for high enough doping, CDW contrast disappears altogether at a negative bias voltage before contrast inversion would actually appear.

![STM Image](image)

Fig. 1 Charge order contrast inversion revealed by STM on 1T-TiSe₂. Top row: 1.4x1.2 nm² bias dependent STM micrographs showing contrast inversion below the Fermi energy. Set parameters of STM data are, from left to right, $V_b$=-300 mV and $I_t$=600pA, $V_b$=-100 mV and $I_t$=100pA, $V_b$=+100 mV and $I_t$=200pA. DFT simulations of the expected STM topographic contrast of the CDW as a function of bias in (middle row) electron doped and in (bottom row) pristine 1T-TiSe₂.

The STM data and DFT simulations of Fig. 1 reveal a remarkable doping dependence of the energy where Cl occurs. The disagreement between experiment and DFT for undoped TiSe₂ is likely to arise from two different sources: first, the well-known problem with DFT underestimating band gaps means that the fine details of the TiSe₂ gap will not be precisely correct; second, the well-known self-doping of TiSe₂ with excess Ti in experiments, which will shift the Fermi level. Bias dependent STM images of the CDW near single atom defects also suggest a doping dependence of the Cl. Most of the area imaged in Fig. 2 does not show any Cl between -100 mV and +100 mV, as already pointed out in Fig. 1. However, there is contrast inversion between these two biases in the right-hand side region of Fig. 2(e) and (f), between the defects marked A and B. The region with inverted contrast is expanding with increasing negative sample bias to encompass most of the field of view at -300 mV (Fig. 2(a)–(d)).

Comparing with DFT simulations, the absence of Cl at opposite biases in the central regions of Fig. 2, away from the defects, is consistent with a globally electron-doped system. The contrast around the defects indicates that the doping is locally modified: while defects C and D behave markedly as electron donors, the presence of Cl near zero bias in the region between defects A and B suggests that they have a light hole-doping character, such that their combined action turns the area towards neutrality. The net effect manifests as an increasing electron doping gradient from defects A and B to defects C and D, with the strongest electron doping character around defect D. The role of defects and bias dependent STM imaging has been discussed previously in 2H-NbSe₂ [11]. However, the focus of that study was on the ability of defects to stabilize the CDW phase near the transition temperature without addressing Cl and local doping effects.
Fig. 2 Doping dependence of the CDW contrast inversion. 10×10 nm² STM topography of 1T-TiSe₂ at (a) -300 mV, (b) -250 mV, (c) -200 mV, (d) -150 mV, (e) -100 mV and (f) +100 mV sample bias. CI happens at an increasingly high binding energy near defects A to D, indicating their different doping nature (see text). Set currents are (a) 600 pA, (b) 300 pA, (c, d and f) 200 pA, (e) 100 pA.

As mentioned in the introduction, there are very few topographic STM studies reporting contrast inversion for any CDW material in the literature. In most cases, the focus has been on comparing images taken at opposite polarities, as would be expected in a classic Peierls transition. Here, we find that images taken at low opposite biases are indeed very similar, while clear CI is observed between images measured at selected negative biases. In the following, we demonstrate that this observation is a direct consequence of a CDW gap opening below \( E_F \) (corresponding to \( V_{\text{bias}}=0 \) V) and shifting to higher binding energy with increasing electron doping.

We first need to show that the observed contrast inversion in the STM micrographs is indeed a CDW feature. To this end, we consider two real space images of the CDW taken at two different biases below \( E_F \). Fig. 3(a) was acquired at a large negative bias, where the periodic pattern reflects the charge accumulation associated with the CDW reconstruction in TiSe₂. Fig. 3(b) was acquired at a smaller negative bias closer to the Fermi level, and shows the corresponding periodic pattern of charge depletion (c.f Fig 1).
Fig. 3 Charge order origin of the contrast inversion observed in bias dependent STM images of 1T-TiSe₂. (a) Negative sample bias image at -250 mV showing the real space distribution of charge accumulation. (b) Negative sample bias image at -100 mV showing the real space distribution of charge depletion. (c) Contrast inversion applied only to the CDW component of the image in (b). (d) Contrast inversion applied to the full image in (b). Set current is 300 pA. Image size is 6x6 nm².

If the differences between the two images in Fig. 3(a) and (b) are due to the CDW, they should be related through an inversion of the periodic charge order reconstruction pattern. To verify this, we manually invert the contrast of the CDW signal of the charge depletion image in Fig. 3(b) in the following way. First, we apply Fourier filtering to separate the signal corresponding to the CDW from the rest of the image. We then invert this CDW image and recombine the result with the rest of the original micrograph (see Methods). The resulting image shown in Fig. 3(c) is in excellent agreement with the experimental charge accumulation image in Fig. 3(a). Alternatively, if we invert not only the CDW component, but the full image, including the atomic lattice contrast in Fig. 3(b), we obtain a completely different topographic pattern unable to reproduce the experimental one (Fig. 3(d)). The contrast difference between the two STM topographies in Fig. 3(a) and (b) is thus definitely due to the CDW contrast inversion.

The doping dependent CI discussed above can be understood by means of a simple one-dimensional model (Fig. 4). Let us consider a BCS-like local density of states (LDOS) [9], with a gap centered at \( E_F \) (Fig. 4(c)) and a harmonic spatial modulation where the states above and below the gap midpoint are spatially 180° degrees out-of-phase (Fig. 4(a)). A constant current STM image amounts to integrating over all states from \( E_F \) up to the imaging bias at each sampling point. Similarly, we integrate the model LDOS in our simulations (Fig. 4(a)) between \( E_F \) and the imaging bias at each position to reconstruct a bias dependent topography (Fig. 4(b)). When the CDW gap is centered on \( E_F \) (Fig. 4(a)), the integration at positive (negative) bias runs over primarily depleted (accumulated) states. In this case, CI (equivalent to a \( \pi \)-shift for a harmonic profile) is expected between any opposite polarity images, as long as CDW contrast is achieved. This can be seen explicitly as a \( \pi \)-phase shift at \( E_F \) (Fig. 4(c)) in the phase as a function of imaging bias of the calculated sinusoidal CDW signal in Fig. 4(b).

Shifting the CDW gap below the Fermi level, as illustrated in Fig. 4(f), completely changes the situation. Here, positive bias STM imaging still involves integration over primarily depleted states as in the absence of a shift. However, imaging up to a finite negative bias corresponding to the middle of the CDW gap \( -V_{\text{mid}} \) will still primarily reflect depleted states (Fig. 4(d)), in contrast to the unshifted case. Hence, the CDW contrast reveals depleted charge regions when imaging at biases between \( -V_{\text{mid}} \) and a finite positive bias, and there will be no CI between opposite polarity images in the range \( \pm V_{\text{mid}} \) (Fig. 4(e), solid and dotted red lines).
Reducing the bias voltage below $-V_{\text{mid}}$, both charge depletion and charge accumulation in the local density of states contribute to the tunneling current. Within the harmonic and symmetric charge redistribution model considered here, the CDW contrast is then progressively reduced to ultimately disappear at a compensation bias voltage $-V_{\text{comp}} = -2V_{\text{mid}}$ (Fig 4(e), dotted black line). Only setting the bias voltage below $-V_{\text{comp}}$ will enable to reveal the CDW pattern corresponding to charge accumulation. Consequently, contrast inversion does not happen at $E_F$, but at a negative bias $-V_{\text{comp}}$ corresponding to

$$\int_{-V_{\text{comp}}}^{-V_{\text{mid}}} \text{LDOS} \cdot dE = \int_{-V_{\text{mid}}}^{0} \text{LDOS} \cdot dE.$$ 

Note that $-V_{\text{comp}}$ can be larger than the maximum negative bias where CDW contrast is still achievable, in which case contrast inversion cannot be observed. This is the case, for example, in Cu intercalated TiSe$_2$ [12]. The actual values of $V_{\text{mid}}$ and $V_{\text{comp}}$ will depend on the detailed material band structure.

![Fig. 4](image)

Fig. 4 One-dimensional model description of the CDW contribution to the STM topography. (a) Spatial and energy dependent CDW LDOS with the CDW gap centered at $E_F$. (b) Corresponding topography traces with inverted contrast between opposite polarity traces, and (c) their bias dependent phases -- contrast inversion happens at $E_F$. (d) Spatial and energy dependent CDW LDOS with the CDW gap shifted below $E_F$. (e) Corresponding topography traces at selected bias voltages and (f) their bias dependent phases -- contrast inversion happens below $E_F$. The solid black line in panel (c) and (f) illustrate the BCS-like model DOS used in the modeling.

The simple 1D model introduced in Fig. 4 reproduces all the experimental CDW features observed by STM on TiSe$_2$. Furthermore, it is perfectly consistent with the rigid band shift moving the CDW gap to higher binding energy as a function of electron doping observed by ARPES [13]. Finding CI at a finite negative sample bias in pristine TiSe$_2$ is consistent with electron doping due to the unavoidable Ti self-doping. The bias dependent contrast observed in Fig. 2 is also consistent with our model assuming electron doping is locally reduced by the presence of defects A and B, resulting in a position dependent band shift. Depending on sample bias and distance from the defects, all three contrast configurations discussed in Fig. 4(e) are observed. Specifically, we see CDW contrast corresponding to charge accumulation regions, to charge depletion regions, and to regions without any CDW contrast corresponding to imaging at $-V_{\text{comp}}$.

This study helps to lift the puzzle of the frequently reported absence of contrast inversion in topographic STM images of the CDW. It also provides an alternative insight on the CDW gap, whose amplitude and position with respect to $E_F$, as determined by scanning tunneling spectroscopy, is still controversial [14]. Our systematic investigation of TiSe$_2$ shows that CI can take place at bias voltages significantly away from the Fermi level, with a remarkable dependence.
on the local doping. This is a direct consequence of the bands and the CDW gap shifting to higher binding energy upon electron doping. In this scenario, we understand the absence of CI in Cu doped TiSe₂ as due to the gap shifting significantly below the Fermi level [12]. Finally, the doping dependent CI we observe by STM poses explicit constraints on any model description of the CDW phase transition. It suggests that the CDW formation involves primarily electronic states away from the Fermi level, which implies that the transition cannot be driven by a particular topology of the Fermi surface. The system gains energy through the momentum dependent electron-phonon and electron-electron interactions, emphasizing the strongly correlated nature of electrons in the CDW phase of TiSe₂.

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**AUTHOR CONTRIBUTIONS**

C.R. designed the experiment. A.S. and M.S. performed the STM measurements. M.S., A.S. and Á.P. performed data analysis. D.B. performed the DFT simulations. Á.P. conceived the one-dimensional model. E.G. synthesized the bulk crystals. Á.P., A.S. and C.R. wrote the paper. All authors contributed to the scientific discussions and manuscript revisions.

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**Methods**

**Crystal growth and STM measurements**

Single crystals of 1T-TiSe$_2$ were grown via iodine vapor transport. A stoichiometric mixture of titanium and selenium was sealed in a quartz ampoule under vacuum. Crystals were subsequently grown at T=590°C for 25 days, to minimize the unavoidable Ti self-doping [15]. We performed scanning tunneling microscopy and spectroscopy using a SPECS Joule-Thomson STM with base temperature of 1.2 K and base pressure below 1×10$^{-10}$ mbar. Tips were made of mechanically cut PtIr and electrochemically etched tungsten wires, with no noticeable differences in the data. Each tip was conditioned in-situ on single crystal Ag(111) or Au(111) surfaces. The TiSe$_2$ single crystals were cleaved in ultrahigh vacuum at room temperature. All the STM data were acquired at 5 K, and negative bias corresponds to probing states below the Fermi level of the sample.

**DFT modelling**

DFT modeling was performed with the plane wave pseudopotential code VASP [16, 17], version 5.3.5. Projector-augmented waves [18] in a 7.01×7.01 Å$^2$ rhombohedral unit cell were used with the Perdew-Burke-Ernzerhof [19] exchange correlation functional and plane wave cutoff of 212 eV. The 1T-TiSe$_2$ surface was modeled with four layers. A Monkhorst-Pack mesh with 9×9×1 k-points was used to sample the Brillouin zone of the cell. The parameters gave an energy convergence better than 0.01 eV. During structural relaxations, a tolerance of 0.03 eV/Å was applied. STM images were generated following the Tersoff-Hamann [20] approach in which the IV characteristic measured by STM is proportional to the integrated local density of states (LDOS) of the surface using the BSKAN code [21]. The effect of doping was simulated by adding a fraction of an electron per unit cell (up to 0.4) with an accompanying uniform positive background.

**Contrast inversion by Fourier filtering**

First, we take the Fourier transform (FT) of the charge depletion image in Figure 3(b) of the main text. This yields a sharp and intense peak structure at the first order Bragg-peaks of the CDW and atomic modulations, and at the linear combinations of these wave vectors (higher harmonics). We use Fourier filtering to separate the signal corresponding to the CDW from the rest of the image. To this end, we mask the most unambiguous CDW components (first order peaks and first order linear combination of them) and suppress the rest of the FT. To obtain the CDW contrast inverted image we inverse transform the masked part of the FT and subtract it twice from the original topographic image.
Extended Data Fig. 1 - DFT simulations as a function of bias and electron doping. Without electron doping (first row) the contrast inversion happens across zero bias. Adding electrons, we find that the contrast distinctive of positive bias images of neutral specimen is now observed at negative biases, at -50 meV for +0.1 e⁻ doping and at -100 meV for +0.2 e⁻ doping per unit cell.