Energy-dependent spatial texturing of charge order in 1T-CuxTiSe2

SPERA, Marcello, et al.

Abstract
We report a detailed study of the microscopic effects of Cu intercalation on the charge density wave (CDW) in 1T-CuxTiSe2. Scanning tunneling microscopy and spectroscopy reveal a unique, Cu-driven spatial texturing of the charge-ordered phase, with the appearance of energy-dependent CDW patches and sharp π-phase shift domain walls (πDWs). The energy and doping dependencies of the patchwork are directly linked to the inhomogeneous potential landscape due to the Cu intercalants. They imply a CDW gap with unusual features, including a large amplitude, the opening below the Fermi level, and a shift to higher binding energy with electron doping. Unlike the patchwork, the πDWs occur independently of the intercalated Cu distribution. They remain atomically sharp throughout the investigated phase diagram and occur in both superconducting and nonsuperconducting specimens. These results provide unique atomic-scale insight into the CDW ground state, questioning the existence of incommensurate CDW domain walls and contributing to understanding its formation mechanism and interplay with superconductivity.

Reference
DOI : 10.1103/PhysRevB.99.155133

Available at:
http://archive-ouverte.unige.ch/unige:116696

Disclaimer: layout of this document may differ from the published version.
Energy-dependent spatial texturing of charge order in 1T-Cu$_x$TiSe$_2$

Supplemental material

Marcello Spera, Alessandro Scarfato, Enrico Giannini and Christoph Renner

Department of Quantum Matter Physics, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

Identification and counting of intercalated Cu atoms in 1T-Cu$_x$TiSe$_2$

The local Cu concentration and the relative occupation of Cu$_{1/4}$ and Cu$_{3/4}$ CDW sites are determined on large scale STM images (Supplemental Fig. 1). Green triangles highlight Ti defects we use to align high and low bias images with atomic-scale accuracy. We first identify Cu atoms at high bias (Supplemental Fig. 1a – black symbols) and then overlay their positions on low bias images where the atomic lattice and the CDW are resolved (Supplemental Fig. 1b). The total number of Cu atoms is 218, in agreement with the nominal concentration $x = 0.02$. Of these Cu atoms, 59 occupy ¼ sites and 159 are on ¾ sites, in close agreement with the expected occupancy of 25% and 75%, respectively.

Supplemental Figure 1: 30x30 nm$^2$ STM micrographs of the same area of Cu$_{0.02}$TiSe$_2$ at 1.2 K. $V_{bias}$ = (a) -1.2 V, (b) -200 mV. The green symbols indicate intercalated Ti defects, black symbols indicate intercalated Cu sites identified at -1.2 V, white and blue symbols indicate which of those correspond to ¼ and ¾ intercalated positions, respectively.
Energy dependent CDW imaging in 1T-TiSe₂

Supplemental Fig. 2 shows the bias dependent CDW contrast of the same region of a TiSe₂ crystal at 1.2 K. The CDW can be well resolved for tunneling biases close to the Fermi level, while for high negative and positive biases (below -400 mV and above +300 mV, respectively) the CDW contrast is highly suppressed. We identify the presence of CDW patches due to charge inhomogeneities also in the pristine crystal, with a much smaller spatial extent and uncorrelated with Ti intercalants (black arrows).

Supplemental Figure 2: Full energy dependence of 17x17 nm² STM micrographs of TiSe₂ at 1.2 K. Bias voltage: (a) -800 mV, (b) -400 mV, (c) -350 mV, (d) -300 mV, (e) -200 mV, (f) -100 mV, (g) 100 mV, (h) 200 mV, (i) 300 mV. Current: 100 pA.
Energy dependent CDW imaging in 1T-Cu$_x$TiSe$_2$

Supplemental Fig. 3 shows the bias dependent CDW contrast of the same region over a broad energy range in Cu$_{0.02}$TiSe$_2$. Starting from high negative bias, STM reveals intercalated Cu atoms (panel a) whose number is in agreement with the nominal doping of the crystal. Increasing the bias voltage, the CDW contrast clearly develops first at the Cu sites (panel c). These patches grow when increasing the bias voltage further and merge to span the entire sample surface when the bias is well inside the CDW gap (panel f). Finally, increasing the tunneling bias above the CDW gap at positive bias, the CDW again forms patches, but at this polarity, they are located and fade last in the Cu poor regions (panel h). The exact same behaviour is observed for Cu$_{0.06}$TiSe$_2$ (Supplemental Fig. 4), with a larger number of Cu atoms compared with the x = 0.02 crystal (panel a), in agreement with the crystal nominal doping x = 0.06.

Supplemental Figure 3: 10x10 nm$^2$ STM images of the same region of Cu$_{0.02}$TiSe$_2$ over a broad bias voltage range at 1.2 K. $V_{bias}$ = (a) -800 mV, (b) -600 mV, (c) -400 mV, (d) -300 mV, (e) -200 mV, (f) -100 mV, (g) 100 mV, (h) 200 mV, (i) 300 mV. $I_{tunnel} = 100$ pA.
Supplemental Figure 4: 7.4x7.4 nm² STM images of the same region of Cu₅₀TiSe₂ over a broad bias voltage range at 5 K. 

$V_{\text{bias}} = (a)\ -800\ \text{mV}, (b)\ -600\ \text{mV}, (c)\ -400\ \text{mV}, (d)\ -300\ \text{mV}, (e)\ -200\ \text{mV}, (f)\ -100\ \text{mV}, (g)\ 50\ \text{mV}, (h)\ 150\ \text{mV}, (i)\ 300\ \text{mV}.$

$I_{\text{tunnel}} = 100\ \text{pA}.$
CDW amplitude measured in superconducting Cu$_{0.06}$TiSe$_2$

The CDW pattern in Cu$_{0.06}$TiSe$_2$ imaged by STM above ($T = 5$ K) and below ($T = 1.2$ K) the superconducting transition temperature $T_c = 3.1$ K remains perfectly unchanged, as unambiguously demonstrated in Supplemental Fig. 5. This result is hinting at a possible coexistence of charge order and superconductivity.

Supplemental Figure 5: 7.4x7.4 nm$^2$ STM micrograph of the CDW in Cu$_{0.06}$TiSe$_2$ ($V_{\text{bias}} = 50$ mV, $I_{\text{tunnel}} = 100$ pA) at (a) 5 K and (b) 1.2 K. The CDW contrast is precisely the same above and below the superconducting transition temperature $T_c = 3.1$ K.
Supplemental Fig. 6 shows additional CDW amplitude analysis on smaller scale STM images of Cu_{0.02}TiSe$_2$. In particular, in the upper half we repeat the analysis shown in Fig. 2 of the original manuscript, for tunneling biases above (+150 mV) and below (-350 mV) the identified CDW gap. In the lower half we show that tunneling closer to the gap edges results in resolving a finite CDW amplitude over the whole investigated surface.

Supplemental Figure 6: a) 11x7.5 nm$^2$ STM micrograph of Cu$_{0.02}$TiSe$_2$ at 1.2 K and V$_{bias}$=150 mV. b) 11x7.5 nm$^2$ STM micrograph of Cu$_{0.02}$TiSe$_2$ at 1.2 K and V$_{bias}$=-350 mV. c) FFT of panel a) d) FFT of panel b). e) CDW amplitude map of panel a). f) CDW amplitude map of panel b). g) RGB sum of panels e) and f). The persistence of green and red domains illustrates the spatial segregation of the CDW domains in panel a) and b). h) 11x7.5 nm$^2$ STM micrograph of Cu$_{0.02}$TiSe$_2$ at 1.2 K and V$_{bias}$=-150 mV. i) 11x7.5 nm$^2$ STM micrograph of Cu$_{0.02}$TiSe$_2$ at 1.2 K and V$_{bias}$=-50 mV. j) FFT of panel h). k) FFT of panel i). l) CDW amplitude map of panel h). m) CDW amplitude map of panel i). n) RGB sum of panels l) and m). The yellow contrast illustrates the absence of spatial segregation of the CDW contrast in panels h) and i).
Supplemental Fig. 7 shows a zoom into one region of Fig. 2b of the original manuscript, emphasising the shift of the CDW wavefronts (dashed lines in panel b) across a πDW.

Supplemental Figure 7: a) 28x28 nm² STM micrograph of Cu\textsubscript{0.02}TiSe\textsubscript{2} at 1.2 K and V\textsubscript{bias}=-200 mV. b) 8x8 nm² area of Cu\textsubscript{0.02}TiSe\textsubscript{2}, taken from a zoom of the gray square of panel a), highlighting the CDW wavefronts (dotted lines) shift across the πDW. On the right-hand side of panel b), all the wavefronts are color-coded in white, while on the left-hand part we change the colors of the wavefronts which undergo a π shift (in green and blue, respectively).