Evolution of the charge density wave in Sulfur substituted 1T-TiSe$_2$

A combined ARPES and STM/STS study

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Motivation
1T-TiSe$_2$ : an intriguing compound

Charge Density Wave
$T_{\text{CDW}} \sim 200$ K, new 2x2x2 structure

Superconductivity
Cu doped 1T-TiSe$_2$

Under pressure

Anomalous resistivity
Ti self-doped 1T-TiSe$_2$

Local resilience of the CDW
In Ti self-doped 1T-TiSe$_2$
B. Hildebrand, PRB, vol. 95, 081104 (2017)
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**Anomalous resistivity**

Sulfur doped 1T-TiSe$_2$

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Influence of Sulfur on the transition temperature and CDW behavior?
STM on $1T$-TiSe$_{2-x}$S$_x$

Real space

The topmost layer of $1T$-TiSe$_2$ is a Se layer.

$V_{\text{bias}} = -1 \text{ V}$

$V_{\text{bias}} = 0.15 \text{ V}$
Characterization of samples $1T$-$\text{TiSe}_2$-$x\text{S}_x$

Identification of S atoms

$V_{\text{bias}} + 0.6 \text{ V, } I_t = 0.15 \text{nA, 15x15 } \text{nm}^2 \text{ at } 4.5 \text{ K}$
Characterization of samples $1T$-TiSe$_{2-x}$S$_x$

Identification of S atoms

$V_{\text{bias}} + 0.6 \text{ V}, I_t = 0.15 \text{nA}, 15 \times 15 \text{ nm}^2$ at $4.5 \text{ K}$
Characterization of samples 1T-TiSe$_{2-x}$S$_x$

Identification of S atoms

Sulfur depletion of ~ 14 pm

$V_{bias} +0.6 \text{ V}$
$V_{bias} +0.3 \text{ V}$
$V_{bias} -0.5 \text{ V}$
$V_{bias} -1.0 \text{ V}$

Topographic effect

$V_{bias} +0.6 \text{ V}$, $I_t = 0.15 \text{nA}$, 15x15 nm$^2$ at 4.5 K
Characterization of samples $1T$-TiSe$_{2-x}$S$_x$

Identification of S atoms

Sulfur depletion of $\sim 14$ pm

DFT simulation*

Measured image

$V_{bias} + 0.6$ V

$V_{bias} + 0.3$ V

$V_{bias} - 0.5$ V

$V_{bias} - 1.0$ V

Topographic effect

14 pm

Se$^{2-}$

S$^{2-}$

* D. R. Bowler, London Centre for Nanotechnology
Characterization of samples 1T-TiSe$_{2-x}$S$_x$

Precise determination of Sulfur concentrations

$x = 0.12$

$V_{bias} + 0.6 \, V$, $I_t = 0.15 \, nA$, 15x15 nm$^2$ at 4.5 K

$x = 0.34$

$V_{bias} + 0.6 \, V$, $I_t = 0.15 \, nA$, 15x15 nm$^2$ at 4.5 K
Characterization of samples 1T-TiSe\(_{2-x}\)S\(_x\)

Precise determination of Sulfur concentrations

\[ \text{Vbias} + 0.6 \text{ V, } I_t = 0.15 \text{nA, 15x15 nm}^2 \text{ at 4.5 K} \]

Ensure negligible Intercalated-Ti concentration
Characterization of samples 1T-TiSe$_{2-x}$S$_x$

Effect of intercalated-Ti

$\sim 1.2 \%$ intercalated-Ti (no sulfur)  
$V_{\text{bias}} \, 0.1 \, \text{V}, \, I_t=0.2\,\text{nA}, \, 17\times17 \, \text{nm}^2 \, \text{at 4.5 K}$

$\sim 2.5 \%$ intercalated-Ti (no sulfur)  
$V_{\text{bias}} \, -0.05 \, \text{V}, \, I_t=0.2\,\text{nA}, \, 17\times17 \, \text{nm}^2 \, \text{at 4.5 K}$

Phase-shifted domains: break of the CDW long-range coherence

B. Hildebrand, PRB, vol. 93, 125140 (2016)

Ensure negligible Intercalated-Ti concentration
Characterization of samples $1T$-$\text{TiSe}_{2-x}\text{S}_x$

Precise determination of Sulfur concentrations

$x = 0.12$

$V_{\text{bias}} + 0.6 \text{ V}, I_t = 0.15 \text{nA}, 15 \times 15 \text{ nm}^2$ at $4.5 \text{ K}$

$x = 0.34$

$V_{\text{bias}} + 0.6 \text{ V}, I_t = 0.15 \text{nA}, 15 \times 15 \text{ nm}^2$ at $4.5 \text{ K}$

Less than 0.2% of intercalated-Ti $\rightarrow$ effects of Sulfur substitution only
Characterization of samples $1T$-TiSe$_{2-x}$S$_x$

Long-range coherence of the CDW

$x = 0.12$

$x = 0.34$

$V_{\text{bias}} + 0.15 \text{ V}, I_t = 0.15 \text{nA}, 15 \times 15 \text{ nm}^2 \text{ at } 4.5 \text{ K}$

Inexistence of phase-slip

Long-range coherence of the 2x2 in-plane electronic modulation

What about ARPES measurements?
ARPES on $1T$-TiSe$_2$

Reciprocal space

Brillouin zone of the 1x1x1 structure

Top view
near-$E_F$ band structure
ARPES on $1T$-TiSe$_2$

Reciprocal space

Brillouin zone of the 1x1x1 structure

Top view near-E$_F$ band structure

T-dependent ARPES study from $T_{\text{ROOM}}$ to 10 K

UPS with He I, $E_{\text{hv}} = 21.2$ eV (close to A and L points)
ARPES on 1T-TiSe$_2$

Reciprocal space

Brillouin zone of the 1x1x1 structure

Top view near-$E_F$ band structure

UPS with He I, $E_{hv} = 21.2$ eV (close to A and L points)

- Se 4p VB at $\bar{\Gamma}$ (Cut $\parallel \bar{\Gamma} - \bar{K}$)

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ARPES on 1T-TiSe$_2$

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Top view
near-$E_F$ band structure

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T-dependent ARPES study from $T_{\text{ROOM}}$ to 10 K

UPS with He I, $E_{\text{hv}}$ = 21.2 eV (close to A and L points)

- Se 4p VB at $\bar{\Gamma}$ (Cut // $\bar{\Gamma} - \bar{K}$)

- Ti 3d CB at $\bar{M}$ (Cut // $\bar{\Gamma} - \bar{M}$ (long axis))
ARPES on 1T-TiSe$_2$

Pristine at RT

Brillouin zone of the 1x1x1 structure

-0.33 eV below $E_F$

Normal phase (RT)
ARPES on 1\textit{T}-TiSe\textsubscript{2}  
CDW phase

Reduced Brillouin zone of the 2x2x2 structure

Top view near-\textit{E}\textsubscript{F} band structure

\textit{\Gamma} \text{--} \text{\bar{M}}
ARPES on 1T-TiSe$_2$

CDW phase

Reduced Brillouin zone of the 2x2x2 structure

Top view
near-EF band structure
ARPES on 1T-TiSe$_2$

Pristine at 10 K

Reduced Brillouin zone of the 2x2x2 structure

Top view
near-EF band structure

CDW phase (10 K)
ARPES on $1T$-TiSe$_2$

Pristine at 10 K

Reduced Brillouin zone of the 2x2x2 structure

Top view near-EF band structure

Semiconductor or semimetal?
ARPES on 1T-TiSe$_2$

Pristine

Se 4p VB slightly below $E_F$

Ti 3d CB above $E_F$

Semiconductor at $T_{\text{ROOM}}$
ARPES on $1T$-TiSe$_2$

Pristine

Normal phase (RT)

CDW phase (10 K)

Se 4p VB slightly below $E_F$

-84 meV

Normal phase (RT)

CDW phase (10 K)

Ti 3d CB above $E_F$

Semiconductor at $T_{\text{ROOM}}$

Doped samples?
ARPES on $1T$-TiSe$_{2-x}$S$_x$

$x = 0.12$

Normal phase (RT)

CDW phase (10 K)

Se 4p VB below $E_F$

Ti 3d CB below $E_F$

Semimetal at $T_{ROOM}$
ARPES on $1T$-TiSe$_{2-x}$S$_x$

$x = 0.34$

Se 4p VB below $E_F$

Ti 3d CB slightly above $E_F$

Semiconductor at $T_{ROOM}$
ARPES on $1T$-TiSe$_{2-x}$S$_x$

$x = 0.34$

Se 4p VB below $E_F$

Ti 3d CB slightly above $E_F$

Normal phase (RT)

CDW phase (10 K)

Semiconductor at $T_{\text{ROOM}}$

Evolution of the gap size with temperature?
ARPES on $1T$-TiSe$_{2-x}$S$_x$

T-dependence Pristine
ARPES on $1T$-TiSe$_{2-x}$S$_x$

T-dependence Pristine

\[ \Gamma \]

\[ \bar{M}/\Gamma^* \]

\[ E_F \]

\[ \vec{k} \]

\[ \vec{k} \]

\[ \bullet = (\times - \circ)^2 \]

Indirect band gap squared
ARPES on $1T$-TiSe$_{2-x}$S$_x$

T-dependence Pristine

Energy gap squared (meV$^2$)

Temperature (K)

Indirect band gap squared

$\bullet = (\times - \bigcirc)^2$
ARPES on $1T$-TiSe$_{2-x}$S$_x$

$T$-dependence Pristine

\[ \Delta^2(T) - \Delta^2(T_C) \propto \tanh^2(A \sqrt{\frac{T_C}{T}} - 1) \]

$T_{CDW} = 220 \text{ K} \pm 5 \text{ K}$

What about the Sulfur doped samples?
ARPES on $1T$-TiSe$_{2-x}$S$_x$

T-dependence S-doped

Indirect band gap squared

$x = 0.12$

$x = 0.34$
ARPES on $1T$-TiSe$_{2-x}$S$_x$

T-dependence S-doped

Indirect band gap squared

$x = 0.12$

$T_{CDW} = 185 \text{ K} \pm 5 \text{ K}$

$x = 0.34$

$T_{CDW} = 195 \text{ K} \pm 5 \text{ K}$
ARPES on $1T$-TiSe$_{2-x}$S$_x$  
T-dependence S-doped

Indirect band gap squared

$x = 0.12$

$T_{CDW} = 185\, \text{K} \pm 5\, \text{K}$

$x = 0.34$

$T_{CDW} = 195\, \text{K} \pm 5\, \text{K}$

Consistent with temperature-dependent resistivity measurements?
Resistivity of $1T$-TiSe$_{2-x}$S$_x$

Transition temperatures from resistivity in agreement with ARPES

$x = 0.12 \quad T_{CDW} = 186$ K

$x = 0.34 \quad T_{CDW} = 193$ K
Summary

STM/STS

\(x = 0.12\)

\(x = 0.34\)

ARPES

\(x = 0.12\)

\(x = 0.34\)

\(T_{CDW} = 185 \pm 5\, \text{K}\)

\(T_{CDW} = 195 \pm 5\, \text{K}\)

\(\rho (T)\)

\(f(T)\)

\(E\)

\(E_F\)

\(\Gamma\)

\(\vec{M}\)

\(\vec{k}\)

\(\text{Normal phase}\)

\(T_{CDW} = 185 \pm 5\, \text{K}\)

\(T_{CDW} = 195 \pm 5\, \text{K}\)
Outlook

- pristine TiSe$_2$ semiconductor
- sulfur lowers $T_{CDW}$ nonlinearly
- slight reentrant behavior for low sulfur concentration

- TiSe$_2$ under pressure becomes semimetallic
- TiS$_2$ is a semiconductor with no CDW

$T_{CDW} = 185 \, K \pm 5 \, K$

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Outlook

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**structural effect of isovalent S substitution**


**Competition between a positive chemical pressure effect and band reconstruction**