Emergence of Fermi pockets in an excitonic CDW melted novel superconductor

D. Qian,1 D. Hsieh,1 L. Wray,1 E. Morosan,2 N.L. Wang,3 Y. Xia,1 R.J. Cava,2 and M.Z. Hasan1

1Department of Physics, Joseph Henry Laboratories of Physics, Princeton University, Princeton, NJ 08544
2Department of Chemistry, Princeton University, Princeton, NJ 08544
3Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

(Dated: 22 November, 2006)

A superconducting (SC) state ($T_c \sim 4.2$K) has very recently been observed upon successful doping of the CDW ordered triangular lattice TiSe$_2$, with copper. Using high resolution photoemission spectroscopy we identify, for the first time, the momentum space locations of the doped electrons that form the Fermi sea of the parent superconductor. With doping, we find that the kinematic nesting volume increases whereas the coherence of the CDW order sharply drops. In the superconducting doping, we observe the emergence of a large density of states in the form of a narrow electron pocket near the $L$-point of the Brillouin Zone with $d$-like character. The $k$-space electron distributions highlight the unconventional interplay of CDW to SC cross-over achieved through non-magnetic copper doping.

PACS numbers: 71.20.Be, 71.30.+h, 73.20.At, 74.90.+n

Charge-density-waves (CDW) and superconductivity (SC) are two of the most fundamental collective quantum phenomena in solids. The competition between the two is one of the central issues of condensed matter physics [1, 2, 3, 4, 5, 6]. A microscopic study of this competition is often difficult for two reasons: one, most systems involve some forms of intervening phases such as the magnetic order observed in the parent state of cuprate or cobaltate superconductors; two, there lacks systematically tunable electronic parameters compatible with microscopic $k$-space imaging techniques such as angle-resolved photoemission spectroscopy (ARPES). Until very recently, no system existed where controlled chemical tuning allowed this competition to be studied in microscopic detail. Recent investigations have shown that upon controlled intercalation of TiSe$_2$ with copper ($Cu_xTiSe_2$) one can systematically tune between a CDW state and a novel superconducting state which emerges near $x = 0.04$, with a maximum $T_c$ of 4.15K reached near $x = 0.08$ [1]. A quantum melting of CDW order was also observed, recently, in the parent compound by pressure [2]. Cu$_x$TiSe$_2$ thus provides a rare opportunity to systematically investigate the quantum phase transition from a CDW ordered state to superconductivity in microscopic detail.

The parent compound TiSe$_2$ has been known since the 1960s and has been extensively studied [8, 9, 10, 11, 12, 13, 14] due to the unconventional nature of the CDW state. In this Letter, we use high resolution ARPES to image the momentum space evolution of doped electrons as they evolve from the undoped CDW ordered phase to an optimal superconductor by copper doping for the first time. A detailed knowledge of momentum space distribution of electronic states is critically important in developing a theory for the superconducting order parameter ($s$, $p$ or $d$-wave) realized in this novel materials class. Based on the emergent Fermi surface topology and momentum-space distinctions of the participant electrons in each phase we directly show that the superconducting phase emerges upon the gradual loss of coherence of the CDW state on the same site; thus the two states compete in a microscopic manner and not due to phase separation or other extrinsic effects. In the superconducting doping we observe the emergence of large density of states in the form of an extremely narrow electron pocket of about 100 meV bandwidth.

Undoped TiSe$_2$ is a layered material with trigonal structure and hexagonal Brillouin zone. From previous high/finite temperature photoemission studies of the undoped material [10], TiSe$_2$ is believed to be either a semimetal or a very small gap semiconductor. It undergoes a $(2\times2\times2)$ structural transition below the CDW transition temperature $T_c=220$K. Upon copper doping, the resistivity anomaly near 200K is suppressed and samples become more metallic-like and eventually superconductors.
FIG. 2: **CDW state melts near superconducting doping**: Low temperature \( T << T_{CDW} \) at \( x=0 \) doping evolution of bands in the vicinity of the \( L \)-point (top row) and the \( \Gamma \) points (bottom row). With increasing copper concentration the intensity of the folded band decreases and spectral weight concentrates near the \( L \)-points in the form of an electron pocket with bandwidth about 0.1 eV. (Bottom row) With increasing doping spectral weight near the \( M-\Gamma-M \) cuts continues to shift to lower energies and the deeper-lying bands tend to split further from each other.

FIG. 3: **Temperature evolution of spectral function**

**with copper doping**

Energy distribution curves for \( k = L+0.1 \ \text{Å}^{-1} \) are shown for \( x=0, 0.04 \) and 0.06 dopings. The peak at 0.25 eV in \( x=0 \) at \( T=20\text{K} \) is due to the band folding. With increasing copper doping the intensity of the 0.25 eV peak drops while the intensity of the quasiparticle peak grows dramatically.

at low temperatures as measured in powder samples \cite{1}. Recently, high quality single crystal samples were grown \cite{16} making \( k \)-resolved measurements possible. ARPES measurements were carried out at beamline ALS-12.0.1 at the Advanced Light Source and SRC-U-NIM beamline at the Synchrotron Radiation Center. The data were collected with 13eV to 79eV photons with better than 10meV to 25meV energy resolution and an angular resolution better than 1% of the Brillouin zone using Scienta analyzers with chamber pressure better than \( 8 \times 10^{-11} \) torr. The \( \Gamma \) and \( L \) points are determined by tracing the band maximum and minimum via changing photon energy \cite{10}. Photon energies of 13eV and 56eV were used for the measurements near the \( \Gamma \)-point whereas 19 and 78eV photons were used for the data collection near the \( L \) point. Cleaving the samples in situ at 20K or 250K resulted in shiny flat surfaces characterized by diffraction to be clean and well ordered with the same symmetry as the bulk. The measured valence band (Figure-1) was found to be in good agreement with LDA band theory \cite{15}.

The low temperature evolution of momentum-resolved electronic structure of TiSe\(_2\) with copper doping is shown in Figure-2. A spectacular change of low-energy electronic structure is observed with systematic doping. The emergence of a pocket like band near the \( L \)-point is very prominent at low temperatures. With copper doping the density of states near the \( L \)-point increases systematically while the states below 0.2 eV are seen to be systematically suppressed. At low temperatures, the states below 0.2 eV near the \( L \)-point are due to the folding of bands from the \( \Gamma \)-point via the 2x2x2 reconstruction which is a consequence of the CDW order. With copper doping, we observe a weakening of the folding strengths in \( x=0.04 \) and \( x=0.06 \) samples. In fact in the \( x=0.06 \) samples folding is extremely weak suggesting a short range nature or near-absence of the CDW order. Figure-2(bottom row) shows the evolution near the \( \Gamma \)-point. A systematic sink-
The prominent peak at 0.25 eV in the vicinity of the L-point. With increasing Cu concentration Fermi level rises up. At the Γ point this is seen as lowering of the Se 4p bands (a-c, top row) and the emergence of low-energy states. At the L-point, doping gives rise to an electron pocket with bandwidth of about 0.1 eV. The L-pocket grows with increasing copper doping.

The high temperature evolution of electronic states near k = L+0.1 Å⁻¹ with doping are shown in Figure-3. The peak grows in intensity and moves to higher binding energies with decreasing temperature. This behavior is consistent with an earlier report on the x=0 samples [12]. With increasing copper doping the intensity of the 0.25 eV peak drops while the intensity or the density of states near the Fermi level grows dramatically.

Above the CDW transition temperature (for T > 220K), in the doped system, we find that the chemical potential is near the midpoint of the leading edge of the quasiparticle peak which is a clear indication that the doped compounds are metals (Fig-2&4). In contrast, the location of the chemical potential in the undoped system is at the peak (highest intensity) suggesting it is either the thermal tail signal from a band that barely grazes the Fermi level.

We have carried out a detailed measurement of electron distribution n(k) in the A-L plane in all metallic samples of Cu_xTiSe_2. The presented data in Figure-5 is shown with an energy integration window of about 20 meV within the Fermi level and was taken in the first quadrant then symmetrized over the Brillouin zone. This is checked by direct measurements in other quadrants and found to be consistent with the symmetrization procedure apart from intensity variations due to changing matrix elements. Large intensities in the form of ellipses are observed at the midpoints of the hexagonal arms. In the superconducting doping samples, Cu_{0.06}TiSe_2, these zone-boundary ellipses resolve as electron-like pockets (Fig-5) which originate from the sinking band near the L-point in Fig-4(bottom row).

With increasing doping the gap closes and low-energy states cross the Fermi level. This leads to the emergence of kinematic nesting instabilities (non-2x2x2 type) along A-L and A-H. Our data show that the CDW state loses long-range coherence with doping but no new superstructure is observed as can be seen by band folding. Such loss of coherence is quite evident from decreasing intensity of the 0.25 eV feature near the L-point (Fig-3).

Within band theory no nesting is expected to generate a 2x2x2 commensurate superstructure for the electron distribution in the x=0 compound [13]. With copper doping we...
find that the electron pocket near $L$-point continues to grow thereby increasing the phase space for nesting but no new band folding is observed and the strengths of 2x2x2 folding continues to drop ruling out nesting as a mechanism for CDW in the doped system.

Following the theoretical suggestion of W. Kohn [17], an electronic (excitonic-like) mechanism recently been proposed to account for the CDW order of the parent compound [13] (and references there-in). If this scenario is correct, one would expect the electron-hole coupling necessary to generate a gap to decrease in the doped systems (which were previously unavailable for study) since the CDW loses long-range coherence with doping. In this scenario, the evidence for the loss of coherence comes from the fact that the bottom of the pocket band at $L$-point (Fig-2(c)/top panel) is not as flat as seen in the undoped compound as reported in ref. [13]. It is unclear if this scenario is supported in the doped systems since no clear recovery of the parabolic-like shape is evident in the doped systems.

Irrespective of the CDW decoherence mechanism, it is well known that increasing density of states (DOS) at the Fermi level, $D(E_f)$, enhances superconducting pairing correlations in a system. The structurally analogous novel superconductor Na$_x$CoO$_2$ exhibits enhancement of $D(E_f)$ with Na doping in the presence of hydration [3]. It is known that $D(E_f)$ also increases in the Fe-doped systems, Fe$_x$TiSe$_2$ and Fe$_x$TiTe$_2$ [3, 14], however no superconductivity is observed in any of these systems. It is likely that the magnetic moments in the Fe$_x$Ti(Se/Te)$_2$ are strong enough to suppress superconductivity via the non-unitary interactions (renormalizing $T_c$ to zero). In Cu$_x$TiSe$_2$, copper is monovalent (Cu$^{+1}$) and non-magnetic (3d$^{10}$ and S=0). Therefore its main role is to donate an electron to the Ti-Se layer which then delocalizes. We have observed in this work that this electron mostly enters the parent band around the $L$-point that has $d$-like (Ti-3d) character which exhibits weak dispersion (less than 100 meV). Therefore, the overall effect of non-magnetic copper doping is to raise the $d$-like density of states, $D(E_f)$, at the Fermi level. Such increases in $D(E_f)$ leads to a rise in $T_c$ in many systems, as expected in the BCS-Eliashberg scenario: $k_BT_c = \hbar\omega_F/(\pi m^*\xi)$.\n
Finally, we note that the Fermi velocity ($v_F$) of the $L$-point electron pocket is about 0.4 ± 0.1 eVÅ (see E vs. k in Fig-4(c)). This allows us to estimate the expected coherence length, $\xi \sim \frac{h\omega_c}{v_F} \sim 29$ nm, under the assumption that this band is the Fermi sea for the superconducting pairing in this compound. This value is remarkably close to the value of 22 nm estimated from $H_{c2}$ measurements [10] for x=0.07 samples which provides further support for our identification of this $L$-pocket electrons taking part in the superconducting pairing in this compound. It is known that the CDW phase of x=0 parent compound is associated with the large softening of an $L$-phonon [18]. It is possible that the $L$-phonon plays a key role in the superconducting mechanism.

In conclusion, we have reported the first measurement of the low-lying states and the Fermi surface topology of the copper doped CDW superconductor. Our results show that an electron-like pocket near the $L$-point continues to grow upon doping into the superconducting phase. A systematic loss of the long-range coherence of the CDW state is observed at low temperatures via the loss of spectral intensity from the folded bands with increasing doping suggesting that the CDW microscopically competes with superconductivity. Momentum space distribution of electronic states is crucial in developing a microscopic theory/mechanism for the superconducting order parameter realized in this novel materials class. The reported evolution of overall electronic structure with copper doping will be further helpful in formulating a theory of CDW-superconductivity competition in general.

This work is primarily supported by DOE grant DE-FG-02-05ER46200. RJC and MZH acknowledges partial support through NSF(DMR-0213706). ALS is supported by the Office of Basic Energy Sciences DOE/DE-AC02-05CH11231; SRC/UW is supported by NSF/DMR-0537588.

[1] E. Morosan et.al, Nature Phys., 2, 544 (2006).
[2] S.A. Kivelson et.al, Nature, 393, 550 (1998).
[3] P.A. Lee et al., Rev. Mod. Phys. 78, 17 (2006); S. Sachdev and S.C. Zhang Science 295, 452 (2002); M. Imada et al., Rev. Mod. Phys. 70, 1039 (1998).

[4] K. Takada et al., Nature 422, 53 (2003); D. Qian et al., Phys. Rev. Lett. 96, 216405 (2006); D. Qian et al., Phys. Rev. Lett. 96, 046407 (2006), also Phys. Rev. Lett. 97, 186405 (2006).

[5] L. Fang et al., Phys. Rev. B 72, 14534 (2005).

[6] D.E. Moncton et al., Phys. Rev. Lett. 34, 734 (1975).

[7] C.S. Snow et al., Phys. Rev. Lett. 91, 136402 (2003).

[8] J.A. Wilson and A.D. Yoffe, Adv. Phys. 18, 193 (1969).

[9] F.J. Di Salvo et al., Phys. Rev. B 14, 4321 (1976).

[10] R.Z. Bachrach et al., Phys. Rev. Lett. 37, 40 (1976); M.M. Traum et al., Phys. Rev. B 17, 1836(1978); G. Margaritondo et al., Phys. Rev. B 23, 3765 (1981); O. Anderson et al., Phys. Rev. Lett. 55, 2188 (1985); N.G. Stoffel et al., Phys. Rev. B 31, 8049 (1985).

[11] Th. Pillo et al., Phys. Rev. B 61, 16213 (2000).

[12] K. Rossnagel et al., Phys. Rev. B 65, 235101 (2002).

[13] T.E. Kidd et al., Phys. Rev. Lett. 88, 226402 (2002).

[14] K. Yamazaki et al., Physica B, 351, 262 (2004); X.Y. Cui et al., Phys. Rev. B 73, 085111 (2006).

[15] A. Zunger et al., Phys. Rev. B 17, 1839 (1978).

[16] E. Morosan et al., cond-mat/0611310 (2006).

[17] W. Kohn, Phys. Rev. Lett. 19, 439 (1967).

[18] M. Holt et al., Phys. Rev. Lett. 86, 3799 (2001).