Disorder Quenching of the Charge Density Wave in ZrTe$_3$

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The charge density wave (CDW) in ZrTe$_3$ is quenched in samples with a small amount of Te isoelectronically substituted by Se. Using angle-resolved photoemission spectroscopy we observe subtle changes in the electronic band dispersions and Fermi surfaces upon Se substitution. The scattering rates are substantially increased, in particular for the large three-dimensional Fermi surface sheet. The quasi-one-dimensional band is unaffected by the substitution and still shows a gap at low temperature, which starts to open from room temperature. Long-range order is, however, absent in the electronic states as in the periodic lattice distortion. The competition between superconductivity and the CDW is thus linked to the suppression of long-range order of the CDW.

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The charge density wave (CDW) is a much studied self-organization of metallic electrons in a crystalline solid [1,2]. Besides electronic signatures it manifests itself as periodic lattice distortion (PLD) with a periodicity given by the CDW modulation. In the last decade, the competition between CDWs and superconductivity (SC) gained renewed attention, following observations of incommensurate PLDs in the copper oxide family of superconductors [3–5]. In a very simple picture a competition between CDW and SC may arise due to the removal of spectral weight from the density of states at the Fermi level (DOS at $E_F$) if an energy gap is formed. Quenching the CDW restores DOS at $E_F$, which is required for SC. If it arises from static disorder this will also affect the SC properties, these have been shown theoretically to be more robust, especially when considering electron correlations [6,7]. In the extreme case of Josephson-linked networks of one-dimensional chain segments, superconductivity is even found to be enhanced by disorder [8].

Besides the complex oxides cited above, competition between CDW and SC exists in simpler binary materials. Quenching of a CDW under pressure and concomitant emergence of SC has been found widely in transition-metal trichalcogenides [9,10], rare-earth trichalcogenides [11–13], and layered transition-metal dichalcogenides [14]. The specific arrangement of electronic bands that form the CDW as well as the PLD varies widely between these materials, thus establishing the competition as a fundamental principle of solid-state physics.

The uniaxial material ZrTe$_3$ shows (filamentary) SC below about $T_c \approx 2$ K at ambient pressure [15,16]. The CDW is detected as an anomaly in resistivity around $T_{CDW} = 63$ K [15] with an incommensurate PLD modulation $\tilde{q}_{CDW} \approx (0.07, 0, 0.333)$ [17]. The resistivity continues to drop in a metallic fashion below $T_{CDW}$. The two main Fermi surface (FS) sheets are a hololike sheet in the $(a,b)$ planes three dimensional (3D) and a pair of electronlike and very flat sheets from quasi-one-dimensional (1D) bands [18–20]. Bulk SC emerges in ZrTe$_3$ when the CDW is quenched, e.g., at hydrostatic pressures above $P_c = 5$ GPa [10] or in disordered samples grown at high temperatures [21]. For the quenching of the CDW under pressure, two potential mechanisms have been discussed: disorder [22,23], or a rearrangement of band fillings in the multisheet FS leading to the loss of the CDW stability [24]. In either scenario it is reasonable to assume that the SC involves electrons in the 1D sheets of the FS that have been identified as driving the CDW [18–20] and which show strong electron-phonon coupling (EPC) to low-energy vibrational modes [25,26]. This electron-lattice interaction probably contributes to stabilizing the long wavelength (small $q$) CDW.

In this Letter, we access the regime of low disorder by light chemical substitution of Te with Se, ZrTe$_{3-x}$Se$_x$. A suppression of the CDW both in transition temperature and magnitude of the resistivity anomaly was reported [27]. Above $x = 0.02$ the CDW anomaly is removed and bulk multiband Bardeen–Cooper–Schrieffer type SC with $T_c$ up

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to 4.5 K emerges; the coupling is dominantly intraband with some interband contributions [27]. With the isoelectronic substitution only a slight rearrangement of carriers between FS sheets is expected. Below, we clarify these subtle changes, including a shift of the van Hove singularity (vHS) in the q1D band to occupied states. Even the slight disorder in a sample of $x = 0.04$, exchanging less than 1.5% of Te, leads to strong and sheet-dependent decreases in electron scattering length. The signatures of fluctuating CDW gaps in both pure and substituted ZrTe$_3$ are observed, with a kink of the temperature dependence when long-range order sets in ZrTe$_3$ and less strong gapping and no kink in ZrTe$_{2.96}$Se$_{0.04}$.

Single crystals of ZrTe$_3$ and ZrTe$_{2.96}$Se$_{0.04}$ have been grown by chemical vapor transport and characterized as described before [27]. For Angel-Resolved Photoemission Spectroscopy (ARPES) measurements, the samples were cleaved at the temperature $T = 7$ K and a vacuum of $10^{-10}$ mbar, exposing (001) surfaces as the samples cleave in the van der Waals gap between layers formed by Te$^{2-}$.Te$^{3+}$ atoms (inset in Fig. 1). ARPES data were acquired at beam line I05-ARPES [28] at $T$ between 7 and 290 K. The photon energy was set to $h\nu = 34$ eV, and the energy resolution was chosen as $\delta E = 7$ meV with an angular resolution of less than 0.2°. The polarization vector was kept in the $(b, c)$ planes of the crystal lattice ($p$ polarized). The $k_x$ and $k_y$ directions correspond to directions along the $b$ axis and approximately the $a$ axis, respectively.

Figure 1 shows two FS maps for samples of pure ZrTe$_3$ and ZrTe$_{2.96}$Se$_{0.04}$. The labeling of high symmetry points acknowledges the effectively two-dimensional electronic state observed in ARPES due to a surface relaxation [29]. This relaxation also leads to a splitting of observed bands, thus complicating the analysis. We selected $h\nu = 34$ eV, at which one component of the split bands dominates the spectra. At different $h\nu$ the same features are seen [29,30], but strong contributions from both components would complicate the peak fitting analysis.

Analyzing the differences between ARPES data from the two samples, first, we discuss the shape and position of bands near $E_F$. Second, we address the scattering rates as observed by peak widths. Finally, we discuss the temperature dependence of spectral weight at $E_F$. At first sight the features of the FS appear very similar, namely the almond shaped central feature, labeled 3D [Figs. 1(a) and 1(c)]. In these maps, the pair of q1D sheets are of low intensity. Close to $\bar{D}$ the intensity is further reduced by the suppression of spectral weight at the chemical potential ($E_F$) at low $T$ [20,29]. Close to $\bar{B}$ at $k_y = \pm 0.2$ Å$^{-1}$ two closing contours of this sheet are nevertheless clearly discernible.

Slicing into momentum distribution curves (MDCs) [Figs. 1(b) and 1(d) for $E = E_F$] reveals differences between the two data sets for the 3D FS sheet. The $k_y$ wave vector along $\bar{\Gamma} - \bar{B}$ is reduced by 4% in ZrTe$_{2.96}$Se$_{0.04}$ when compared to ZrTe$_3$. The $k_x$ Fermi wave vector $k_F$ along $\bar{\Gamma} - \bar{Y}$ is increased by 2%. Most remarkably, the $k_F$ of the q1D bands close to $\bar{D}$ are found to be identical within the error bars between both samples [Fig. 1(d)]. The $k_F$ are summarized in Table I. The anisotropy of the 3D sheet is thus slightly reduced, and the FS volume is decreased in ZrTe$_{2.96}$Se$_{0.04}$ when compared to ZrTe$_3$. From this reduction of FS volume we can estimate a reduction of hole-type carrier numbers in the 3D band of about 2%.

From the easily observable $k_F$ values along $k_y$ (“q1D”) at $k_x = 0.2$ Å$^{-1}$ and “q1D$_{YP}$” at $k_x = 0.8$ Å$^{-1}$), the two q1D bands appear completely unchanged by the Se substitution. A close look is provided by the dispersion maps in Figs. 2(a)–2(h). In Figs. 2(b) and 2(f) we trace the dispersion of the two bands along $k_y$ by numerical fits. The summarized results in Fig. 2(k) reveal a decrease of the energy $E$ of this band by $-0.012$ eV at $\bar{B}$. This results in a drastic change of the spectra at $\bar{B}$, marked by arrows in Figs. 2(a) and 2(e) and shown in Fig. 2(i). In pure ZrTe$_3$, this very sharp peak has been assigned to a vHS at $E_F$ [20]. In ZrTe$_{2.96}$Se$_{0.04}$, the vHS is shifted to occupied states and
larger in ZrTe due to EPC increases from zero at Material[30]. The widths are composed of two main these widths with details given in the Supplemental results of MDC peak widths as a function of CDW formation.

We now turn to the analysis of scattering rates. The mechanism of sharpening the peak at low T [20] does not come into effect. In agreement with the shift of the lower q1D band, $k_F$ of the upper q1D band is also reduced from $k_x = 0.2$ Å$^{-1}$ in ZrTe$_3$ to $k_x = 0.13$ Å$^{-1}$ in ZrTe$_{2.96}$Se$_{0.04}$. Thus, the estimated shift of the upper q1D band (−50 meV at $k_F$) is larger than the shift of the lower q1D band (−12 meV).

At $\bar{D}$ the peak position of the bottom of the q1D band is identical while the step height of intensity at $E_F$ is larger in ZrTe$_{2.96}$Se$_{0.04}$ [Fig. 2(j)]. The T dependence of this intensity will be analyzed below for further insight into CDW formation.

We now turn to the analysis of scattering rates. The results of MDC peak widths as a function of $E$ are shown in Fig. 3. Standard numerical fitting was used to determine these widths with details given in the Supplemental Material [30]. The widths are composed of two main contributions: a constant width due to impurity scattering plus an energy-dependent width due to EPC. The width due to EPC increases from zero at $E = E_F$ [31,32] and saturates, in our data around $E - E_F = −0.01$ eV, which matches the range of phonons with strong EPC in ZrTe$_3$ [25,26]. For example, a pronounced width increase to 0.025 Å$^{-1}$ from 0.013 Å$^{-1}$ is observed at position “3D$_{TY}$” for ZrTe$_3$ [Fig. 3(a)]. Along $k_y$, at “3D$_{TB}$” as well as q1D (at $k_x = 0.2$ Å), the data for ZrTe$_{2.96}$Se$_{0.04}$ show significantly higher widths throughout when compared to ZrTe$_3$ [Figs. 3(b) and 3(c)]. Near the $D$ point q1D$_{YD}$ we find basically identical data for both samples [Fig. 3(d)]. We note that error bars of the data from ZrTe$_{2.96}$Se$_{0.04}$ are generally larger than ZrTe$_3$ due to slightly different data acquisition settings. We consider the deviation of the two data sets at q1D$_{YD}$ very close to $E_F$ as insignificant because the data points are compatible within these error bars. Thus, the extrapolated widths at $E_F$ due to defect scattering are summarized in Table I. When multiplied with the Fermi velocity $v_F$, they give an estimate of the scattering rate $1/\tau$ due to disorder. The scattering rate is enhanced upon Se substitution except for position q1D$_{YD}$ of the strongly nested CDW band [33].

Analyzing the intensity at $E_F$ as a function of $T$ (Fig. 4) we find near constant values for the 3D band (not shown) as well as for q1D near $k_x = 0.2$ Å$^{-1}$ (apart from a spurious lower intensity data point in ZrTe$_{2.96}$Se$_{0.04}$ at the lowest $T$). This is regular behavior of the Fermi-Dirac distribution function without any modification of the bands or spectral weight. At $\bar{B}$, ZrTe$_3$ shows an upturn of intensity at low temperature, which is not observed in ZrTe$_{2.96}$Se$_{0.04}$, thus confirming the relation of this effect to the vHS [20,34]. Near $\bar{D}$ the drop of intensity sets in at room temperature in

| Location | Character | $2k_F$ (Å$^{-1}$) | $\delta k$ (Å$^{-1}$) | $v_F$ (eV · Å) | $1/\tau$ (eV) | $2k_F$ (Å$^{-1}$) | $\delta k$ (Å$^{-1}$) | $v_F$ (eV · Å) | $1/\tau$ (eV) |
|----------|-----------|-----------------|----------------|--------------|-------------|----------------|----------------|--------------|-------------|
| “3D$_{Y}$” | Zr $d_1$ | 0.633 (3) | 0.013 (3) | 4.0 (2) | 0.05 (1) | 0.622 (5) | 0.025 (5) | 4.5 (2) | 0.11 (2) |
| “3D$_{TB}$” | Te(1) $p_z$, Zr $d_1$ | 0.232 (2) | 0.026 (4) | 1.8 (2) | 0.05 (1) | 0.244 (3) | 0.050 (9) | 2.1 (2) | 0.10 (2) |
| q1D | Te(3) $p_z$ | 0.12 (2) | 0.02 (1) | 4.8 (9) | 0.10 (5) | 0.13 (2) | 0.04 (1) | 6.4 (9) | 0.26 (7) |
| q1D$_{YD}$ | Te(2) $p_z$ | 0.086 (1) | 0.05 (2) | 8.9 (5) | 0.44 (20) | 0.085 (1) | 0.03 (2) | 9.2 (5) | 0.28 (18) |

FIG. 2. ARPES dispersion cuts for ZrTe$_3$ (a)–(d) and ZrTe$_{2.96}$Se$_{0.04}$ (e)–(h) at $T = 7$ K. Red dots in panels (a), (b), (e), (f) show the peak positions determined by numerical fits. A detailed view of these peak positions for the q1D bands along $k_x$ close to $\bar{B}$ is shown in panel (k). Energy distribution curves at high symmetry points are shown in (i) for $\bar{B}$ and in (j) for $\bar{D}$ for both samples. Dashed lines in panel (k) are drawn following the intensity traces in panels (b), (f) as a guide to the eye.
both samples and far above the structural transition $T_{\text{CDW}}$ in ZrTe$_3$. Thus, both samples show the gap signature of fluctuating CDW [20]. In ZrTe$_3$, the gapping is strong with a 50% depletion of spectral weight at $E_F$ at low $T$, and the $T$ dependence shows a kink when long-range order sets in. In ZrTe$_{2.96}$Se$_{0.04}$, this $T$ dependence is near linear [Fig. 4(b)] and the depletion is less strong than in ZrTe$_3$. The quenching of long-range order of the CDW is also confirmed by the absence of a PLD in x-ray diffraction from ZrTe$_{2.96}$Se$_{0.04}$ down to $T = 20$ K [30].

The orbital composition of the various bands has previously been analyzed in detail in Ref. [18]. The dominant orbital character and contributing atoms are summarized in Table I, and graphical representations are reproduced in the Supplemental Material [30]. Near $\bar{D}$ (point $D$ or $E$ of the bulk Brillouin zone), the q1D band is formed almost exclusively from Te $p_x$ orbitals of the atoms Te$^{(2)}$ and Te$^{(3)}$ (orbitals oriented along the $a$ axis of the lattice). At $\bar{B}$ (bulk point $B$ or $A$) and in the close vicinity of this point, significant contributions come from $p_y$ orbitals of all three Te atoms, including Te$^{(1)}$. The 3D FS sheet is similarly composed of strong contributions from $p_y$ orbitals of Te$^{(1)}$ as well as Zr $d$ orbitals. The observation of a large increase of scattering rates close to $\bar{B}$ and in the 3D FS sheet may thus arise from preferential incorporation of Se impurities in the Te$^{(1)}$ site. Alternatively, the pure one-dimensional character of the $p_x$-derived band near $\bar{D}$ may show suppressed defect scattering due to the phase space being reduced to only forward or full backscattering [35].

In either case we note that the effects of the disorder are much more pronounced in the bands that show no gapping due to CDW formation, while the CDW-gapped portions of the FS are the locations of little change between ZrTe$_3$ and ZrTe$_{2.96}$Se$_{0.04}$. This region of the Brillouin zone was shown to couple strongly to phonons [26]. Our data show this EPC directly in several locations of momentum space by an increase of peak widths with decreasing $E$ in the range of typical phonon energies. The EPC is similar in both samples and of similar magnitude as typical two-dimensional metals [31].

In conclusion, we find that the quenching of long-range CDW order with light isoatomic substitution in ZrTe$_{2.96}$Se$_{0.04}$ is driven by a decrease in the static scattering length. Our measurements thus confirm the structural disorder as the primary tuning parameter which dictates the phase diagram of ZrTe$_{3-x}$Se$_x$. The effects of disorder in the electronic spectral function are found to be sheet dependent, detected as a significant increase in the line widths of the 3D band and the q1D bands near $\bar{B}$, while no measurable additional broadening was found near $\bar{D}$. In addition, more subtle band shifts are observed, including a shift of the vHS at $B$ away from the Fermi level to occupied
states. These band shifts are not considered as driving forces of the CDW quenching. A continuous partial loss of DOS around $\bar{D}$ as a function of $T$ is interpreted as a signature of a fluctuating CDW as in previous work [20]. This is expected to weaken the SC and the shift of the vHS will also reduce the DOS at $E_F$ when compared to ZrTe$_3$. The reduction of DOS from the region around $D$ is less strong in ZrTe$_2$Se$_{0.04}$ than in ZrTe$_3$ and lacks the kink signature of long-range order that is observed in ZrTe$_3$. Thus, SC can emerge despite CDW fluctuations.

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