Multiband nodeless superconductivity near the charge-density-wave quantum critical point in ZrTe$_{3-x}$Se$_x$*

Shan Cui(崔珊)$^1$, Lan-Po He(何兰坡)$^1$, Xiao-Chen Hong(洪晓晨)$^1$, Xiang-De Zhu(朱相德)$^{2,4}$, Cedrim Petrovic$^4$, and Shi-Yan Li(李世燕)$^{1,3,4}$

$^1$ State Key Laboratory of Surface Physics, Fudan University, Shanghai 200433, China
$^2$ High Magnetic Field Laboratory, Chinese Academy of Sciences and University of Science and Technology of China, Hefei 230031, China
$^3$ Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China
$^4$ Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA

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It was found that selenium doping can suppress the charge-density-wave (CDW) order and induce bulk superconductivity in ZrTe$_3$. The observed superconducting dome suggests the existence of a CDW quantum critical point (QCP) in ZrTe$_{3-x}$Se$_x$ near $x \approx 0.04$. To elucidate the superconducting state near the CDW QCP, we measure the thermal conductivity of two ZrTe$_{3-x}$Se$_x$ single crystals ($x = 0.044$ and 0.051) down to 80 mK. For both samples, the residual linear term $\kappa_0/T$ at zero field is negligible, which is a clear evidence for nodeless superconducting gap. Furthermore, the field dependence of $\kappa_0/T$ manifests a multigap behavior. These results demonstrate multiple nodeless superconducting gaps in ZrTe$_{3-x}$Se$_x$, which indicates conventional superconductivity despite of the existence of a CDW QCP.

Keywords: superconductivity, charge-density-wave order, thermal transport measurement, gap structure

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1. Introduction

Charge-density-wave (CDW) order usually exists in some low-dimensional materials, especially those transition-metal chalcogenides.[1–4] When the CDW order is suppressed by doping or pressure, a list of them can be tuned to superconductors.[5–8] In the temperature–doping ($T$–$x$) or temperature–pressure ($T$–$p$) phase diagram, sometimes a superconducting dome is observed on top of a CDW quantum critical point (QCP).[5–8] The reminiscent of this kind of phase diagram to that of the heavy-fermion and high-$T_c$ cuprate superconductors raises the possibility of unconventional superconductivity caused by CDW fluctuations.[5–9]

ZrTe$_3$ is such a compound in which the CDW order and superconductivity compete and coexist.[10] It belongs to a family of trichalcogenides $MX_3$ ($M = $ Ti, Zr, Hf, U, Th, and $X = $ S, Se, Te). The structure consists of infinite $X$–$X$ chains formed by stacking $MX_3$ prisms.[11] The polyhedra are arranged in double sheets and stacked along the monoclinic $c$ axis by van der Waals forces.[11] Pristine ZrTe$_3$ itself harbors filamentary superconductivity with $T_c \sim 2$ K.[10] The CDW vector $q \approx (1/14, 0; 1/3)$ is developed in ZrTe$_3$ below $T_{CDW} \sim 63$ K.[12] Like other CDW materials, pressure and doping can melt the CDW order and stabilize its superconductivity to bulk.[13–16] Recently, isovalent substitution of Se for Te was also found to cause a superconducting dome in the ZrTe$_{3-x}$Se$_x$ system, with maximum $T_c = 4.4$ K at the optimal doping $x = 0.04$.[17] It was suggested that this superconductivity may be mediated by quantum critical charge fluctuations.[17] To clarifying the underlying pairing mechanism, it is important to know the superconducting gap symmetry and structure.

Ultra-low-temperature heat transport is an established bulk technique to probe the superconducting gap structure.[18] The existence of a finite residual linear term $\kappa_0/T$ in zero magnetic field is an evidence for gap nodes.[18] The field dependence of $\kappa_0/T$ may further give support for a nodal superconducting state, and provide information on the gap anisotropy, or multiple gaps.[18]

In this paper, we measure the ultra-low-temperature thermal conductivity of ZrTe$_{3-x}$Se$_x$ single crystals near optimal doping to investigate whether the superconducting state is unconventional. The negligible $\kappa_0/T$ in zero field and the rapid field dependence of $\kappa_0(H)/T$ in low field strongly suggest multiple nodeless superconducting gaps in ZrTe$_{3-x}$Se$_x$. In this sense, the superconductivity in ZrTe$_{3-x}$Se$_x$ is likely conventional.

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†Corresponding author. E-mail: shiyan_li@fudan.edu.cn

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2. Experiment

The ZrTe$_3$–Se$_x$ single crystals were grown by iodine vapor transport method.$^{[13,17]}$ Two single crystals from different batches, both with nominal composition $x = 0.04$, were used for this study. Their exact compositions were determined by wavelength-dispersive spectroscopy (WDS), utilizing an electron probe microanalyzer (Shimadzu EPMA-1720). The dc magnetization was measured at $H = 20$ Oe, with zero-field cooling, using a SQUID (MPMS, Quantum Design). The samples were cleaved and cut to rectangular bars, with typical dimensions of $2.12$ mm $\times$ $1.01$ mm $\times$ $0.030$ mm. The largest surface is $ab$-plane. The contacts were made directly on the sample surfaces with silver paint, which were used for both resistivity and thermal conductivity measurements. The contacts are metallic with typical resistance $200$ m$\Omega$ at $2$ K. The in-plane thermal conductivity was measured in a dilution refrigerator, using a standard four-wire steady-state method with two RuO$_2$ chip thermometers, calibrated in situ against a reference RuO$_2$ thermometer. Magnetic fields were applied along the $c$ axis and perpendicular to the heat current. To ensure a homogeneous field distribution in the sample, all fields were applied at temperature above $T_c$.

3. Results and discussion

According to the WDS results, the actual Se contents of the two ZrTe$_3$–Se$_x$ single crystals are $x = 0.044$ and $0.051$, respectively. Below we will use the actual $x$. Figure 1(a) presents the normalized dc magnetization of ZrTe$_2$$_{956}$Se$_{0.044}$ and ZrTe$_2$$_{949}$Se$_{0.051}$ single crystals. The $T_c$ defined by the onset of diamagnetic transition is $4.0$ K for both samples. The significant diamagnetic response confirms that the superconductivity is stabilized to bulk from the filamentary superconductivity in pristine ZrTe$_3$, which is consistent with the previous report.$^{[17]}$ This bulk superconductivity will be further supported by our thermal conductivity data in this study.

Figure 1(b) shows the in-plane resistivity $\rho(T)$ of ZrTe$_2$$_{956}$Se$_{0.044}$ and ZrTe$_2$$_{949}$Se$_{0.051}$ single crystals. No anomaly is observed in the normal state, suggesting the complete suppression of CDW state in them.$^{[17]}$ Fitting the normal-state resistivity data below $60$ K to $\rho(T) = \rho_0 + AT^n$ gives residual resistivity $\rho_0 = 2.82$ $\mu$$\Omega$-$\text{cm}$ and $21.5$ $\mu$$\Omega$-$\text{cm}$ for the $x = 0.044$ and $0.051$ samples, respectively. The resistive superconducting transition at low temperature is plotted in Fig. 1(c). The $T_c$ defined by $\rho = 0$ is $4.06$ K and $3.87$ K for the $x = 0.044$ and $0.051$ samples, respectively. Both of them are near the optimal doping in the phase diagram of ZrTe$_3$–Se$_x$, and the $x = 0.051$ sample is slightly overdoped.$^{[17]}$

To determine their upper critical fields $H_{c2}$, the low-temperature resistivity of these two samples under magnetic fields was also measured. Figures 2(a) and 2(b) show the low temperature $\rho(T)$ curves of ZrTe$_2$$_{956}$Se$_{0.044}$ and ZrTe$_2$$_{949}$Se$_{0.051}$ single crystals under various fields. With increasing field, the superconducting transition is gradually suppressed to lower temperature, and the magnetoresistance in the normal state is very weak. The $H_{c2}(T)$, defined by $\rho = 0$ in Figs. 2(a) and 2(b), is plotted in Fig. 2(c) for both $x = 0.044$ and $0.051$ samples. From Fig. 2(c), we roughly estimate $H_{c2}(0) \approx 1.40$ T and $0.85$ T for them, respectively.

![Fig. 1](color online) (a) The normalized dc magnetization of ZrTe$_2$$_{956}$Se$_{0.044}$ and ZrTe$_2$$_{949}$Se$_{0.051}$ single crystals, measured in $H = 20$ Oe with zero-field-cooled (ZFC) process. (b) The in-plane resistivity of ZrTe$_2$$_{956}$Se$_{0.044}$ and ZrTe$_2$$_{949}$Se$_{0.051}$ single crystals. No anomaly is observed in the normal state, suggesting the complete suppression of CDW state. (c) The resistive superconducting transition at low temperature. For clarity, the resistance of the $x = 0.044$ sample is magnified by five times. The $T_c$ defined by $\rho = 0$ is $4.06$ K and $3.87$ K for $x = 0.044$ and $0.051$ samples, respectively.
The temperature dependence of in-plane thermal conductivity for ZrTe$_2$946Se$_0$044 and ZrTe$_2$956Se$_0$051 single crystals in zero and applied magnetic fields is shown in Fig. 3, plotted as $\kappa/T$ vs. $T$. The thermal conductivity at very low temperature can usually be fitted to $\kappa/T = a + bT^{-\alpha-1}$.\cite{19,20} The two terms $aT$ and $bT^{-\alpha}$ represent contributions from electrons and phonons, respectively. The power $\alpha$ is typically between 2 and 3 due to the specular reflections of phonons at the boundary.\cite{19,20} One can see that all the curves in Fig. 3 are roughly linear, therefore we fix $\alpha$ to 2. In zero field, the fittings give $\kappa_0/T = 0.008 \pm 0.008$ mW K$^{-2}$ cm$^{-1}$ and $0.009 \pm 0.002$ mW K$^{-2}$ cm$^{-1}$ for the $x = 0.044$ and 0.051 samples, respectively. Such a tiny $\kappa_0/T$ in zero field is negligible for both samples. As $T \to 0$, since all electrons become Cooper pairs for the s-wave nodeless superconductors, there are no fermionic quasiparticles to conduct heat. Therefore there is no residual linear term of $\kappa_0/T$, as seen in V$_3$Si.\cite{19} However, for the unconventional superconductors with nodes in the superconducting gap, the nodal quasiparticles will contribute a finite $\kappa_0/T$ in zero field.\cite{18} For example, $\kappa_0/T = 1.41$ mW K$^{-2}$ cm$^{-1}$ for the overdoped cuprate Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2201), a d-wave superconductor with $T_c = 15$ K.\cite{21} For the p-wave superconductor Sr$_2$RuO$_4$, $\kappa_0/T = 17$ mW K$^{-2}$ cm$^{-1}$.\cite{22} Therefore, the negligible $\kappa_0/T$ of the $x = 0.044$ and 0.051 samples suggests that the superconducting gap of ZrTe$_2$$_x$Se$_3$ is nodeless. Note that the negligible $\kappa_0/T$ in zero field also supports the bulk superconductivity in our samples.

When applying field, $\kappa/T$ gradually increases with increasing field, as seen in Fig. 3. In $H = 0.5$ T, the fittings give $\kappa_0/T = 8.27 \pm 0.08$ mW K$^{-2}$ cm$^{-1}$ and $1.14 \pm 0.03$ mW K$^{-2}$ cm$^{-1}$ for the $x = 0.044$ and 0.051 samples, respectively. These values roughly meet their Wiedemann–Franz law expectations $L_0/\rho_0$ ($L_0$ is the Lorenz number $2.45 \times 10^{-8}$ W Ω K$^{-2}$ and $\rho_0$ is the sample’s residual resistivity). The verification of the Wiedemann–Franz law in the normal state shows the reliability of our thermal conductivity measurements. The bulk $H_c^2(0) \approx 0.5$ T is taken for both samples, which is lower than those determined from the resistivity measurements.

![Fig. 2](image-url) (color online) Low-temperature resistivity of (a) ZrTe$_2$946Se$_0$044 and (b) ZrTe$_2$956Se$_0$051 single crystals under various magnetic fields. (c) Temperature dependence of the upper critical field $H_c^2(T)$ defined by $\rho = 0$ in panels (a) and (b). The dashed lines are guide to eye, which point to $H_c^2(0) \approx 1.40$ T and 0.85 T for $x = 0.044$ and 0.051 samples, respectively.

![Fig. 3](image-url) (color online) Low-temperature in-plane thermal conductivity of (a) ZrTe$_2$956Se$_0$044 and (b) ZrTe$_2$956Se$_0$051 single crystals in zero and magnetic fields. The lines are fits of the data to $\kappa/T = a + bT^{-\alpha}$, with $\alpha$ fixed to 2. The dashed lines represent the normal-state Wiedemann–Franz law expectations $L_0/\rho_0$ for the $x = 0.044$ and 0.051 samples, respectively.
To gain more information of the gap structure in ZrTe$_2$$_9$Se$_{0.044}$ and ZrTe$_2$$_9$Se$_{0.051}$, we check the field dependence of their $\kappa_0/T$. The normalized $\kappa_0/T$ as a function of $H/H_{c2}$ is plotted in Fig. 4. For comparison, the data of the clean s-wave superconductor Nb,\cite{23} the multiband s-wave superconductor NbSe$_2$,\cite{24} and an overdoped sample of the d-wave superconductor TI-2201 are also plotted.\cite{21} The slow field dependence of $\kappa_0/T$ in low field for Nb manifests its single isotropic superconducting gap. In Fig. 4, the curves of the $x = 0.044$ and 0.051 samples are similar to that of NbSe$_2$, a multiband s-wave superconductor with the gap ratio $\Delta_l/\Delta_s \approx 3$.\cite{24} This suggests that ZrTe$_{2.3}$Se$_x$ also has multiple nodeless superconducting gaps. Previously, an \textit{ab initio} calculation of the band structure for ZrTe$_3$ at ambient pressure gave a central rounded 2D Fermi surface sheet and two flatter q1D sheets.\cite{8} Therefore, the observation of multiple nodeless superconducting gaps in ZrTe$_{2.3}$Se$_x$ system is not surprising.

Theoretically, it has been shown that unconventional superconductivity with $d_{xy}$ symmetry can appear in close proximity to a charge-ordered phase, and the superconductivity is mediated by charge fluctuations.\cite{25,26} Since the $d_{xy}$-wave gap has line nodes, our results clearly rule out this kind of unconventional superconductivity in ZrTe$_{2.3}$Se$_x$. In this context, the superconductivity in ZrTe$_{2.3}$Se$_x$ is likely conventional. Similar situation happens in the Cu$_x$TiSe$_2$ system. Thermal conductivity measurements suggested conventional s-wave superconductivity with a single isotropic gap in Cu$_{0.06}$TiSe$_2$, near where the CDW order vanishes.\cite{27} So far, the evidence for unconventional superconductivity induced by CDW fluctuations in real materials is still lack. The experiments on more systems with superconductivity near a CDW QCP are needed.

4. Conclusion

In summary, we have measured the ultra-low-temperature thermal conductivity of ZrTe$_2$$_9$Se$_{0.044}$ and ZrTe$_2$$_9$Se$_{0.051}$ single crystals, which are near the optimal doping in the phase diagram of the ZrTe$_{2.3}$Se$_x$ system. The absence of $\kappa_0/T$ in zero field for both compounds gives strong evidence for nodeless superconducting gap. The field dependence of $\kappa_0(H)/T$ further suggests multiple nodeless gaps in ZrTe$_{2.3}$Se$_x$. Unconventional superconductivity with line nodes is excluded in this trichalcogenide system although there is a CDW QCP. It is likely that the superconductivity in ZrTe$_{2.3}$Se$_x$ is still conventional.

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Fig. 4. (color online) Normalized residual linear term $\kappa_0/T$ of ZrTe$_2$$_9$Se$_{0.044}$ and ZrTe$_2$$_9$Se$_{0.051}$ single crystals as a function of $H/H_{c2}$. Similar data of the clean s-wave superconductor Nb,\cite{23} an overdoped d-wave cuprate superconductor TI-2201,\cite{21} and the multiband s-wave superconductor NbSe$_2$,\cite{24} are also plotted for comparison.